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FUNDAMENTAL STUDIES AND ANALYTICAL APPLICATIONS
OF THE DUAL LASER IONIZATION TECHNIQUE

By

Francis Michael Curran

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1983

154-0725

ABSTRACT

FUNDAMENTAL STUDIES AND ANALYTICAL APPLICATIONS OF THE DUAL LASER IONIZATION TECHNIQUE

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Laser-enhanced ionization (LEI) is a recently developed flame spectrometric technique for the analysis of trace metals in flames. In the LEI experiment the analyte is laser-promoted into an excited state. This selectivity enhances the collisional ionization rate of the analyte, and the subsequent ionization signal is collected by a set of biased probes. Dual laser ionization (DLI) is a modification of this technique in which a separate laser is used to ionize the analyte after the resonant excitation step. Under proper conditions this can substantially reduce the collisional dependence of the ionization signal and significantly enhance signal magnitudes. In the studies reported here, a nitrogen laser is used both to pump the dye laser used to resonantly excite the analyte and to provide the ionizing beam. The pulsed nature of this laser system necessitates gated integration.

Four major aspects of the DLI technique are considered in order to characterize the technique more completely. First, the energetics involved in the ionization processes in both LEI and DLI are discussed and compared in order to

determine in which instances DLI can be used effectively to improve the ionization signals obtained with LEI. A close match between ionizing beam photon energy and the difference in energy between the excited state level and the ionization continuum (i.e. the energy defect) is found to be the major factor involved in signal enhancement.

The dependence of the ionization signal on laser power in both LEI and DLI is examined. A simple two level model is developed to describe experimental results. It is shown that in cases where DLI enhancement is observed, further enhancement could have been obtained with a more powerful ionizing beam.

The LEI technique has been shown to be adversely affected by electrical interferences caused by easily ionized components in the sample matrix. This type of interference is discussed with respect to the DLI technique. As in LEI, electrode positioning is found to be very important to signal recovery.

Finally the application of the DLI technique to real sample analysis is described. Results consistent with those obtained in atomic absorption experiments are presented to illustrate the analytical utility of the technique.

To Mom, to Dad, and to Shelley

ACKNOWLEDGMENTS

Simple acknowledgment of Professor S.R. Crouch for his guidance as research director is quite insufficient here. In addition to being a scientist who has taught the author much, he has been a true friend. Thanks go to Professor John Allison for his work as second reader and for his stinging wit. I am also indebted to Professors George Leroi and Paul Hunt for the many hours they spent in scientific discussion with me.

The help and **patience** of Marty Rabb, Dr. Tom Atkinson and Russ Geyer were greatly appreciated. Thanks also go to Dick Menke, Ben Stutsman and Deak Watters in the Machine Shop and to Ron Haas and Scott Sanderson in the Electronics Shop as they were all instrumental in the completion of this work. Margy Lynch, friend and typist, and Naomi Hack, who kept me well fed, informed and awake, were also very helpful.

The author expresses his gratitude to the Department of Chemistry and to the Dow Chemical Corporation for providing financial support.

In my years at MSU I have been lucky enough to meet and work with a number of people who have become my close friends. I doubt a better group could be found anywhere.

Thanks to Rob and Jan, Charlie, Gene, Rytis, Lynn, John, Phil, Hugh, Scott, Pete, Bruce, Nelson, Tony, Pat, Kieth, Paul, Max and Bob. Special mention must be made of Pat Ronan, Clay Calkin, Jim Gano, Susan Alden and April Lockner; although my liver wishes I had never met you, my heart does not. Special thanks also must go to Marguerite Danna (?) and Kim Ratanathanawongs (???). I am sorry to leave you at John's mercy but at least now you are safe from flying fruit and sneak attack.

Finally, I would like to thank my wife, my cats and my family for their warmth and support. The love you all have shown me has been much more than I have deserved (even if I did color well, Auntie).

Bo Schembechler is also gratefully acknowledged. Four U of M victories over MSU have saved one loudmouth a lot of grief.

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CHAPTER I

INTRODUCTION

A. Overview of the Opto-galvanic Effect.

The irradiation of an analyte-containing sample reservoir (most commonly a flame or discharge plasma) by a light source at a wavelength corresponding to a resonant transition of the analyte may yield an observable opto-galvanic signal. The opto-galvanic effect (OGE) is produced by a change in the ionization rate within the sample cell and can be detected by measuring a change in some electrical property of the cell such as its resistance, conductance or the ion current detected by biased probes. The first observation of the OGE was made by Foote and Mohler in 1925¹. They used space-charge amplification in a thermionic diode to detect the ionization of Cs at resonant wavelengths below the photoionization threshold. Their light source was a tungsten lamp, and a monochromator was used for wavelength selection. Shortly thereafter, Penning measured the change in current through a neon discharge tube upon irradiation by another neon discharge².

Although these early experiments pointed out the existence of the phenomenon, little activity in the field of opto-galvanic spectroscopy occurred over the next 50 years because of the limited signal magnitudes obtainable with conventional light sources. This changed with the introduction of tunable dye lasers into the laboratory. Lasers gave spectroscopists convenient and versatile light sources with spectral irradiances capable of saturating many atomic transitions, especially in the visible region of the spectrum. The OGE, with laser excitation, was introduced in experiments at the National Bureau of Standards^{3,4} and in the Netherlands^{5,6}. Observations of the effect in flames has been termed laser-enhanced ionization (LEI); in the recent past it has become one of the most sensitive means available for the detection of trace metals in flames⁷⁻¹⁴. Briefly, in LEI, the absorption of resonant laser photons lowers the energy necessary for ionization and selectively increases the collisional ionization rate of the analyte. The increase can be measured by a set of biased probes placed near the laser irradiated region of the flame. Electrical detection is the major advantage of LEI; the usual limitations of conventional optical detection, such as finite solid angle of collection optics, quantum efficiencies less than unity, and scattered light, are absent.

Recently, we introduced a related technique called dual laser ionization (DLI) in which a second laser beam

provides the energy necessary for ionization from the energy level populated by a dye laser¹⁵. The second laser decreases the collisional dependence of ion formation by providing direct photoionization in some cases. The DLI method shows promise in both trace metal determinations and flame diagnostic studies¹⁵⁻¹⁷. The characterization of the DLI technique is the major focus of this dissertation.

B. Overview of Dissertation

A detailed account of the development of LEI and other related laser-based ionization techniques (e.g. resonance ionization spectroscopy (RIS)) from their inception to the middle of 1982 has been given recently by Lin¹⁸. In addition, most of the following chapters include introduction sections which detail the pertinent background information. Because of this, the historical discussion that immediately follows this section centers on developments from 1982 to the present and reviews earlier developments only briefly.

Chapter II describes the experimental system used to obtain the data presented in the main body of the dissertation. An overview of the system points out the types of signals generated and rationalizes the equipment used. The sections that follow contain more detailed information on specific components.

The next four chapters describe the studies which were performed to characterize the DLI technique. Chapter III elucidates the efficacy-determining aspects of DLI ionization schemes. This begins with a review of the ionization mechanisms common to laser atomic spectroscopy and includes a presentation of pertinent rate equations. Results from experimental studies of atomic Li, Na, K, Ca, Sr, In and Cs in an H_2-O_2 -Ar flame are then presented followed by a discussion of the experimental and theoretical aspects of the enhancements obtained upon addition of the ionizing beam. Strategies for optimizing the technique are also included.

Chapter IV presents studies of the dependence of the ionization signal on laser power in both LEI and DLI. A simple two level model is developed to explain experimental results. Optimization of the DLI signal with respect to laser power is discussed.

Chapter V presents a study of interferences in DLI. Electrical interferences caused by easily ionized matrix components have been a major problem in LEI; this chapter explores the nature of the interferences observed and the methods to avoid them. Some physical interferences which are encountered are also discussed.

In Chapter VI, the DLI technique is extended to a more analytically useful air-acetylene flame. The experiments described, with Ca as an analyte, serve not only to show the utility of DLI as an analytical technique, but also to

test a computerized boxcar integration and data acquisition system designed and built by J. Stanley¹⁹.

Finally in Chapter VII, the work is summarized and recommendations for future studies are made in the hope that future workers can make the technique more generally useful.

There are three appendices to the main body of the dissertation. The first involves discussion of basic DLI characteristics and presents early results obtained with C.A. van Dijk and K.C. Lin. Appendix II details the dye laser alignment procedure developed for the present experimental system. The final appendix contains details of the design, construction and testing of an inexpensive yet versatile lock-in amplifier, useful over the 1-10,000 Hz frequency range. This amplifier was constructed to be used with a commercial atomic absorption unit and may also find application in future atomic emission studies complementary to DLI.

C. Historical

Two articles reintroduced the OGE with laser excitation in 1976^{3,4}. One of these detailed the detection of metal species in flames with biased probes. This technique has become known as laser enhanced ionization (LEI). The other paper described galvanic detection of optical absorptions of laser light by species contained in a discharge tube. Since this date, research in the field of

opto-galvanic spectroscopy (OGS) has been split fairly evenly between experiments in which these two types of sample cells are used as both Lin¹⁸ and Goldsmith and Lawler²⁰ have pointed out in their recent reviews.

C-1. The Opto-galvanic Effect in Non-flame Cells

Goldsmith and Lawler²⁰ have noted that non-flame OGS can be used in experiments requiring either moderate or high (Doppler-free) resolution. In moderate resolution experiments, typically, a single laser is operated at the resonant frequency of some species contained in a discharge. This produces an OGE which is then measured by observing the change in voltage across the discharge or the change in current through the discharge ballast resistor. Both modulated continuous wave (CW) lasers with lock-in detection and pulsed lasers with gated detection have been used to detect atomic²¹⁻²³ and molecular²⁴⁻²⁵ species. Many modifications of this basic experimental design were made between 1976 and 1982. For example, Suzuki used a pick-up coil to observe laser-induced current changes across radio frequency discharges of N₂, Ar, NH₃ and NO₂²⁶. Numerous authors have used more than one laser to step sequentially from one atomic transition to another and thus to examine high lying excited states²⁷⁻³⁰. This type of excitation has also been used in LEI and will hereafter be referred to as stepwise excitation. Though early studies mainly emphasized the examination of

fundamental processes in the discharge, numerous practical applications were found. One of the earliest was the use of the OGE by Green, et al. to frequency lock a CW dye laser³¹. Similarly, Smith and Moffat used the OGE to frequency stabilize a CO₂ laser³². Keller, et al.³³ and Palmer et al.³⁴ have discussed the use of the OGE in wavelength calibration. In more recent studies the OGE has been used to frequency lock CO₂³⁵⁻³⁷, He-Ne³⁸ and tunable diode³⁹ lasers. Dovichi and co-workers have continued work on wavelength calibration of pulsed lasers using the OGE in uranium hollow cathode lamps⁴⁰. Along this same line, two groups have discussed the use of the OGE in spectroscopic line profile measurements and in wavelength calibration. Bachor and co-workers found opto-galvanic and absorption measurements to be similar under proper experimental conditions⁴¹. They also found a nonlinear relation between integral measurement and oscillator strength for Ca. Piepmeier and Beenan followed up an earlier paper on line profile distortion in OGE measurements⁴² with a similar paper on saturation and prefilter effects⁴³.

Both color center and tunable diode lasers operating in the infrared have been used quite extensively to study Rydberg transitions in atomic species⁴⁴⁻⁴⁷ and rovibronic levels in molecules⁴⁸.

Early mechanistic studies by Keller and Zalewski⁴⁹ indicated that direct collisional ionization following resonant laser excitation is not the major mechanism involved in opto-galvanic signal production in hollow cathode lamps. Instead, they suggested that absorbed laser energy is transferred to the electron gas in the discharge and then equally distributed throughout the discharge. Recently, Dreze and co-workers have performed very elegant experiments which have supported the above hypothesis⁵⁰. In these experiments emission from all species (even the Xe fill gas) was found to increase upon irradiation of a uranium hollow cathode with laser light resonant with a U(I) transition. Also, excitation of uranium ions caused intensity increases in atomic uranium emission lines. These findings also indicate that isotope separation using the OGE in hollow cathode lamps is likely to be impossible, a conclusion supported by further experiments described in the same work. This does not, however, rule out completely isotope enrichment in other plasmas in which this type of energy redistribution does not occur. Kushner has recently discussed this topic for the case of Cu in a Cu-Ne positive column discharge⁵¹. Other recent mechanistic studies include metastable quenching in a He discharge⁵² and collisional mixing in a Ne discharge⁵³.

Several miscellaneous experiments have also been performed. Transitions in HCO have been studied in an rf

discharge by Vasudev and Zare⁵⁴. Electron photodetachment from I^- has been studied in an iodine discharge⁵⁵ to obtain electron affinities. Also, two-color, double resonance spectroscopy has been recently applied to the study of highly excited states in the NO molecule in a gas cell⁵⁶.

Intermodulation techniques are usually used in Doppler-free high resolution spectroscopy. With opto-galvanic detection this has been termed IMOGS. Typically, a single laser beam is split, and the two beams are chopped at different frequencies (f_1 and f_2). These beams are then directed to counter propagate in a discharge. If the wavelength is tuned across a resonance of interest and lock-in detection is used at the sum frequency ($f_1 + f_2$), the Doppler-free opto-galvanic signal is observed (cf. 20 and references therein). Rotating polarizers have also been used in place of choppers⁵⁷. Another method for obtaining Doppler-free spectra involves absorption of two photons to excite a one-photon forbidden transition. The laser beam is reflected back upon itself through the discharge so that Doppler effects cancel. This technique has been termed TOGS (cf. 20,58). Recent studies in this area have expanded these techniques. Transitions in N_2 discharges have been studied by two groups. Suzuki and Kakimoto have studied Rydberg states in N_2 using IMOGS with an rf discharge⁵⁹. Miyazaki, et al., used two separate CW lasers,

one a ring dye laser modulated at 550 Hz and the other a linear dye laser modulated at 825 Hz, to obtain the Doppler-free spectra⁶⁰. Zeeman splitting has also been observed with opto-galvanic detection. In one experiment, researchers simply used the IMOGS technique with a hollow cathode discharge immersed in a magnetic field⁶¹. In another a single laser beam modulated at one frequency was used to irradiate a discharge in a magnetic field modulated at another frequency. The opto-galvanic signal measured by a phase sensitive detector operating at the sum frequency showed the sought-after Zeeman splittings⁶².

C-2. Laser Enhanced Ionization (LEI)

As stated previously, the first observation of the opto-galvanic effect in a flame was made in 1976³. The basic principles of the LEI technique have been described in a number of publications since this time^{7,8,11,20,63-67}. Briefly, a laser is tuned to excite at a resonant frequency of a species contained in a flame cell. This selectively increases the ionization rate of that species, and this increase is detected by a set of biased probes near the irradiated volume of the flame cell. The first study was performed using a chopped CW dye laser and Na as the analyte. Following this, three studies appeared in succession, each advancing the state of the art. In each study, flashlamp pumped dye lasers were used to increase the spectral irradiance and the tuning range. The first¹⁴

indicated that excellent detection limits were obtainable if the excited state to ionization continuum energy defect was small. In this study only visible wavelengths were used. The next publication⁶⁸ provided a more detailed mechanistic approach and examined both resonant and non-resonant transitions under saturated and nonsaturated conditions. The number of elements detected by LEI was also expanded through the use of a frequency doubling option in the dye laser. In the third study¹³ a sensitivity factor dependent on the atomization efficiency, laser spectral irradiance, energy defect and the Boltzman population of the lower level of the laser excited transition was developed. Once again the number of elements studied was increased.

One of the major advantages of the LEI technique is its freedom from such optical interferences as scattered light. It does, however, suffer from electrical interferences caused by easily ionized matrix components. These interferences were characterized by Green and co-workers with respect to matrix composition, flame composition, probe voltage and electrode shape⁶⁹. One of their suggestions was the use of plate rather than rod cathodes for increased collection efficiency. Plate electrodes were subsequently examined in more detail by Havrilla and Green⁷⁰. A later study of matrix interference reduction was performed by Turk⁷¹ who showed that a water cooled

cathode near the laser irradiated volume (ie. immersed in the flame) was far superior to external cathodes. In this same time period Trask and Green reported the effects of acid matrices⁷². More recently it has been shown that CW excitation is effective in decreasing matrix effects⁷³. Pulsed signal collection has also been tried, but found ineffective in matrix interference reduction⁷⁴. This same study suggested that time resolution could be used to discriminate against interferences in some cases. For this to be possible the analyte must reach its steady state concentration in the flame more quickly upon nebulization than does the interferent.

To improve sensitivity and selectivity in LEI further, especially for high IP elements for which single laser excitation leaves a large energy defect, stepwise excitation schemes have been devised and tested. In 1979 both the NBS group and researchers in Russia published results of experiments involving stepwise excitation^{10,12}. The NBS group used two dye lasers simultaneously pumped by a single nitrogen laser to produce stepwise excitation of seven elements. The Russians used a Nd:YAG laser to pump two dye lasers in a study of sodium. Later, the Russian groups published results of studies similar to the one described above, but with Li, Cs^{75,76} and In⁷⁷ as the analytes. The NBS group switched to Nd:YAG pumped dye lasers with frequency doubling so that high ionization

potential elements with strong resonant transitions in the ultraviolet could be studied for the first time⁹. Processes related to ion collection in LEI have been studied extensively both theoretically and experimentally. Schenck et al. used a CW dye laser with an opto-acoustic modulator to study spatial and temporal characteristics in a hydrogen/air flame⁷⁸. Another group used two nitrogen-pumped dye lasers to study electron pulse shapes in experiments with sodium⁷⁹. In similar studies, masses and sizes of small particles in flames have been estimated from mobility measurements⁸⁰, and the mobilities of atomic ions have been studied⁸¹.

The OGE has also been used to study molecular species in flames. In the earliest studies, transitions in LaO, SeO and YO were examined using a nitrogen pumped dye laser⁸². These experiments involved single photon excitation followed by collisional ionization and proved that LEI is a viable method for studying molecular transitions in flames. Further work in molecular spectroscopy has involved photo- rather than collisional-ionization and is discussed in the next section.

C-3. Dual Laser Ionization (DLI) and Resonance Ionization (RIS)

Resonance ionization spectroscopy (RIS) is the name given to resonance enhanced photoionization performed in rarified atmospheres (eg. proportional counters). This

has been comprehensively reviewed by Hurst et al.⁸³. In this article schemes for the ionization of almost every atom in the Periodic Table were suggested. Experimental methods were also detailed for studying the mutual diffusion of gases, absolute measurements of atomic excited state densities, absolute photoionization cross-sections and rare events (such as fission fragment detection). Recently, RIS schemes have been used extensively in both atomic and molecular determinations, but very few of these experiments have involved opto-galvanic detection. In most cases mass spectroscopy has been coupled with RIS. For atomic analysis this has been termed resonance ionization mass spectroscopy (RIMS) and has been used by a number of authors (cf. 84 and references therein). For molecular species the term resonance enhanced multiphoton ionization or REMPI has become common. This technique has been discussed in detail in a recent overview⁸⁵. In fact, the only recent coupling of RIS and opto-galvanic detection has been in the study of trace impurities in solids. In this technique, called laser ablation resonance ionization spectroscopy (LARIS), one laser is used to vaporize part of a target sample in a proportional counter. A second laser, tuned to a resonance of the impurity is used to give the RIS signal⁸⁶.

Dual laser ionization is basically the extension of the RIS technique to the flame cell. This was first

introduced by van Dijk, et al. in 1981¹⁵. It should be noted that the stepwise ionization LEI studies performed by the Russian groups (see preceding discussion) were initially intended to be DLI experiments. In each case an ionizing beam (either the Nd:YAG fundamental or one of its harmonics) was used. No DLI enhancement was observed because the stepwise dye laser excitation left the atoms under study in highly excited states from which collisional ionization dominated photoionization (see Chapter III).

Lin and co-workers have recently used the DLI technique to determine flame temperatures¹⁹, and the spatial resolution available with the technique has been found to be useful in circumventing electrical interferences¹⁶. Also recently, rate equations have been used by two different authors to calculate ionization yields in DLI under common experimental conditions^{18,87}.

Atomic species have not been the only focus of the DLI technique. The multiphoton ionization of NO, through a two photon resonance, has been observed with opto-galvanic detection⁸⁸. Comparison of experimentally obtained and computer generated data led to flame temperature estimations. In this same publication relative concentration measurements were used to deduce flame chemistry in different areas of the flame. Two photon photoionization, through a single photon resonance, has also been observed for both the NO⁸⁹ and the PO⁹⁰ molecules.

Finally, both atomic oxygen⁹¹ and hydrogen⁹² have been observed in flames using resonant two photon excitation followed by one photon photoionization.

CHAPTER II

EXPERIMENTAL

A. Overview

Figure 2-1 shows a simplified schematic diagram of the experimental system used to produce DLI and LEI signals. In a typical experiment a solution containing an analyte is introduced into the flame through a pneumatic nebulizer. A nitrogen-pumped, tunable dye laser is focused into the flame to provide resonant excitation. For DLI experiments a portion of the nitrogen (N_2) laser beam is used to provide the energy necessary for ionization. This is directed to the flame so that it is temporally and spatially coincident with the dye laser. The ions, formed by the laser pulses, which occur on the nanosecond (ns) time scale, are collected by a set of biased probes immersed in the flame near the laser-irradiated region. A diagram of the signal collection circuit is shown in Figure 2-2. The electric field between the probes causes the migration of the ions; this migration is mobility-controlled and ion transit times from the ion formation region to the probes are on the order of microseconds (μs). Once collected, the ion signal is amplified by a fast current amplifier. The low duty cycle of the signal

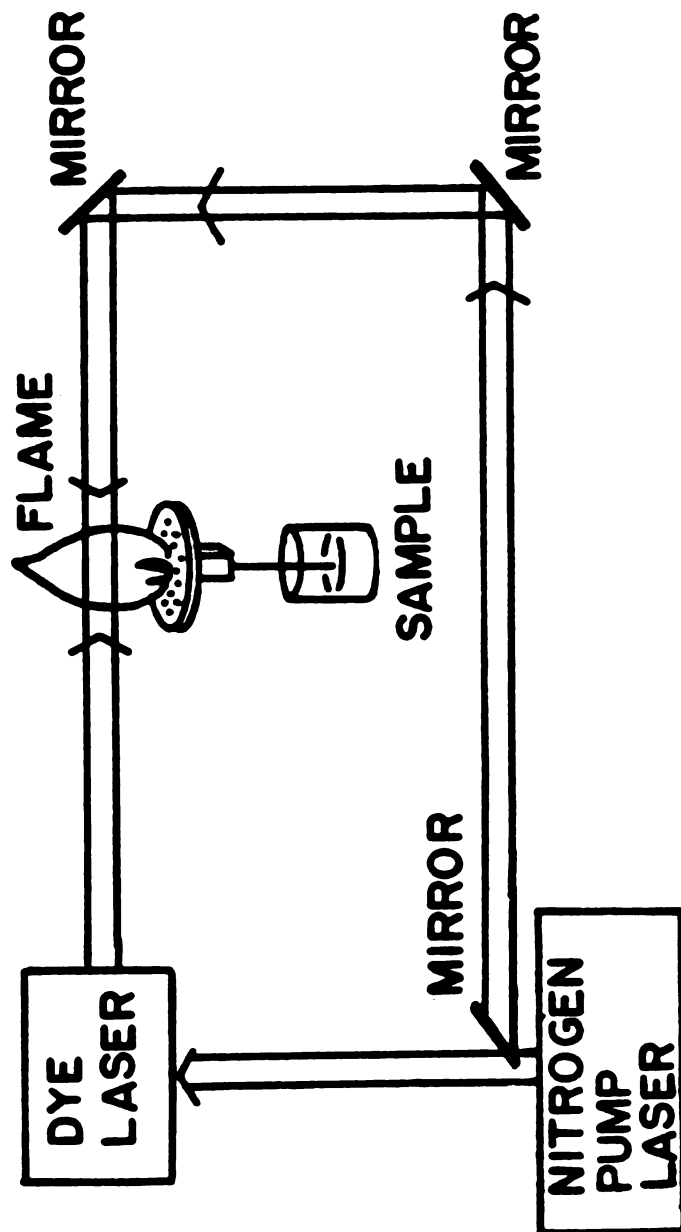


Figure 2-1. Simplified schematic of LEI/DLI system.

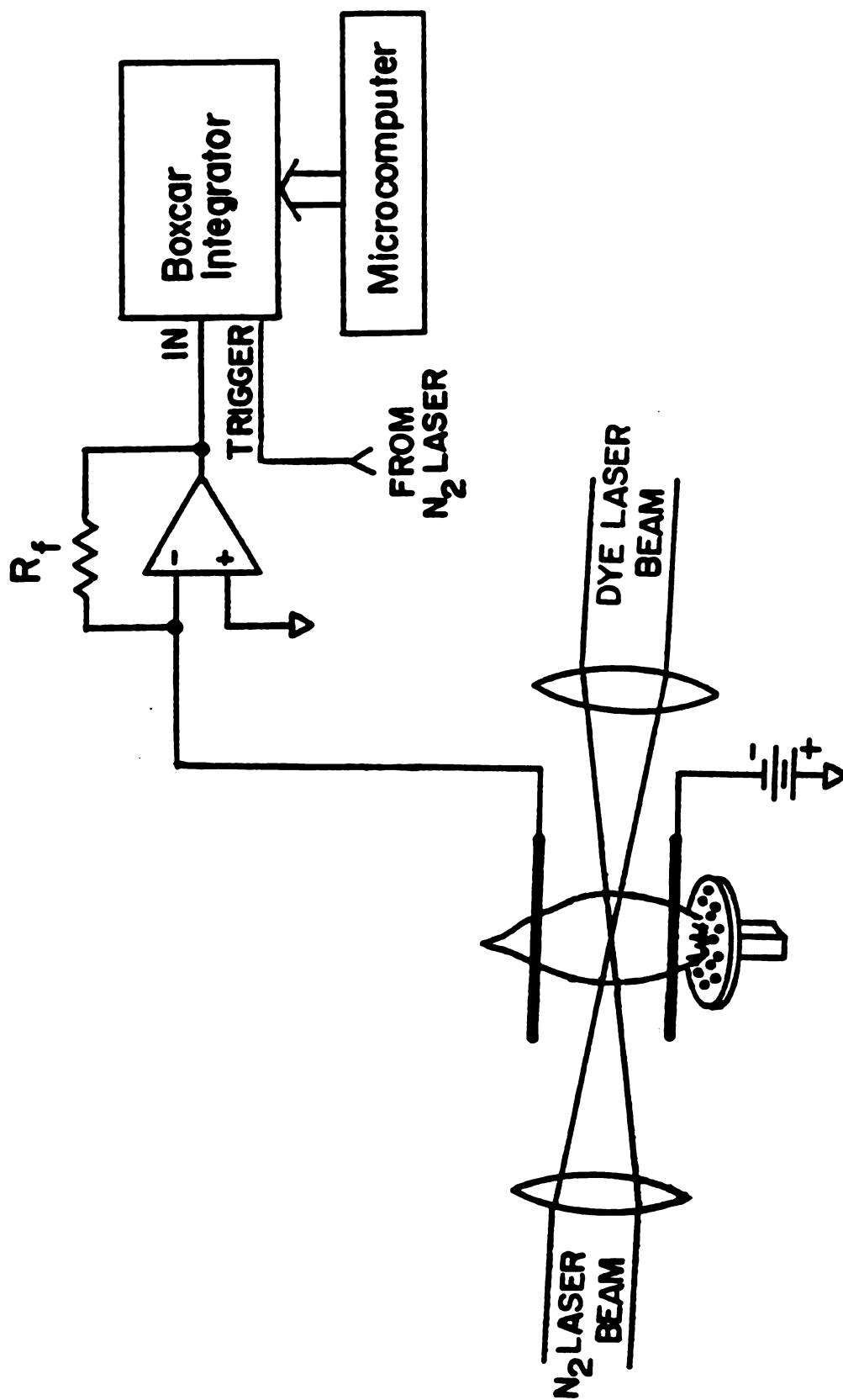


Figure 2-2. Block diagram of ionization signal collection circuit.

necessitates the use of gated integration to improve the signal-to-noise ratio. The output of the current amplifier is the input to a boxcar integrator. The output of the integrator is then either taken to a strip chart recorder for display or to a microprocessor for further processing. A typical time-resolved ionization signal is shown in Figure 2-3.

B. Laser System

The N₂ laser (model 0.5-150, NRG, Inc., Madison, WI), used both as a pump source for the tunable dye laser and as the ionizing beam in DLI experiments, has been described in detail elsewhere¹⁸ so only its general characteristics are listed here. The rated peak power output of the N₂ laser at a repetition rate of 60 Hz is 500 kW. Repetition rates from single pulse to 60 Hz are available (typically a 20 Hz repetition rate was used). The portion of the beam split off and used for ionization had a radiant power between 100 and 150 kW.

The major disadvantage of the N₂ laser as a pump source is the radio frequency interference (RFI) broadcast when breakdown of the spark gap occurs. This introduces noise to all of the associated electronics. To minimize RFI at the source, the N₂ laser was placed in a Faraday cage made of 0.5 mm copper plating. It was also found that keeping the spark gap clean was effective in minimizing RFI. A strict cleaning schedule was adopted.

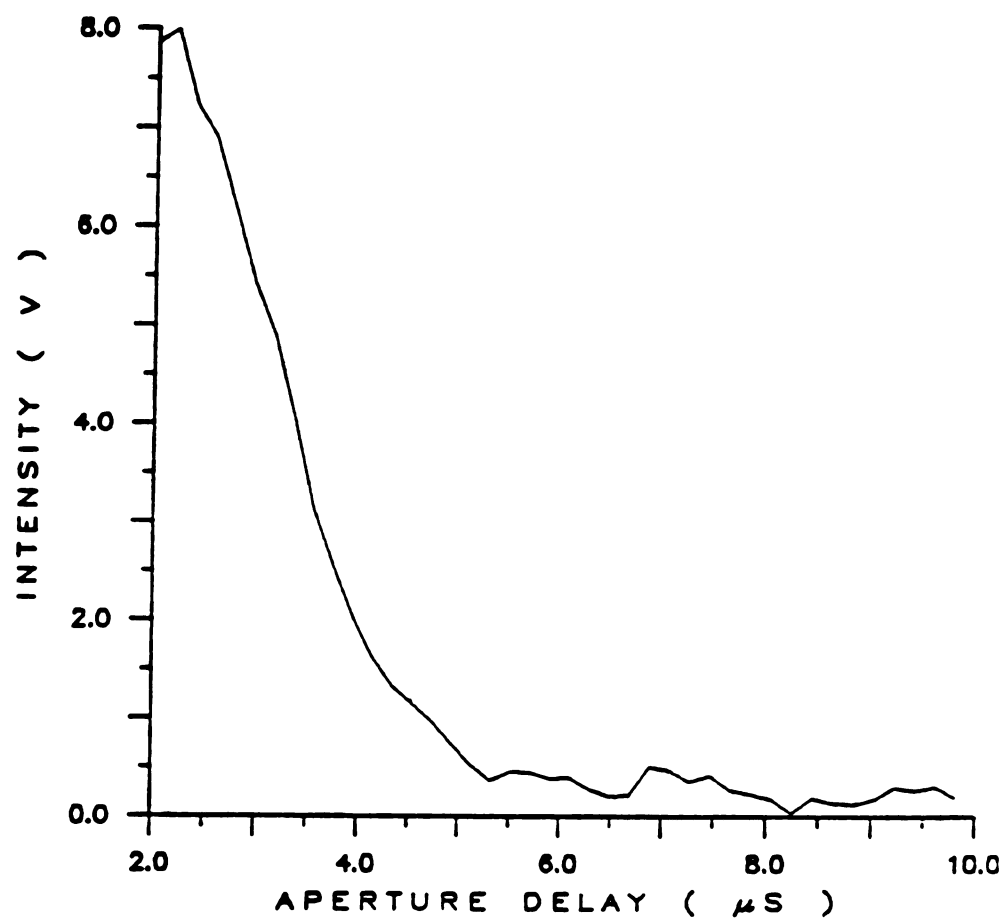


Figure 2-3. Typical time-resolved ionization signal (Na as analyte).

After each 50 hours of use the electrodes were removed and replaced. Replacement electrodes were copied from the originals by the departmental machine shop.

Usually the laser tube pressure was maintained at 72 Torr while the spark gap pressure varied between 22 and 28 psi; this depended upon the length of time since the last spark gap cleaning. To avoid short term variations in the tube and spark gap pressures a dual stage pressure regulator (Model 580, Airco, Inc., Murray Hill, NJ) was used.

The Hänsch type laser system⁹³ along with the alignment procedure developed in our laboratory is described in Appendix B. A list of the dyes used along with their wavelength ranges and typical peak output powers is given in the next chapter. The spectral bandwidths of three of the dyes were checked. Rhodamine 6G was studied by scanning the dye to obtain the fluorescence excitation profile of the Na D line at 589.0 nm. The atomic line width in the flame is small compared to the dye laser bandwidth so the full width-at-half-maximum (FWHM) of the profile represents the bandwidth of the laser. For both Coumarin 460 and DCM a more direct approach was taken. The dye laser output was directed to the entrance slit of a monochromator (to be described in a following section) and observed with a photomultiplier (RCA, 1P28A). The entrance slit of the monochromator was fixed at a value small enough to insure that the bandpass

of the monochromator was small compared to the laser bandwidth. The wavelength counter was set for the wavelength of the analyte resonant transition typically used with that dye in DLI experiments. The dye laser was then scanned around this wavelength. In all experiments the bandwidth was approximately 0.075 nm.

The temporal overlap and pulse shapes of the N_2 and dye lasers are shown in Figure 2-4. They were obtained with a PIN photodiode in a circuit to be described in a later section. The output of the photodiode circuit was displayed on an oscilloscope (Model 564, Tektronix, Inc., Beaverton, OR) equipped with a Polaroid camera (Model C-12, Tektronix, Inc., Beaverton, OR).

Laser power attenuation was accomplished with a set of metal neutral density (ND) filters. These are described in Chapter IV.

C. Flame Systems and Sample Introduction

A laminar flow, premixed, H_2 - O_2 -Ar flame was used in most experiments. This flame is similar to one designed by Lijnse, et al.⁹⁴ and has been described in detail by both van Dijk⁹⁵ and Lin¹⁸. Lin's description includes a full discussion of the advantages of this type of flame and a flow diagram of our particular system. Thus, these are discussed only briefly here. Both central and mantle flames were burned from a Meker burner head. The gases were controlled by dual stage regulators at the tanks,

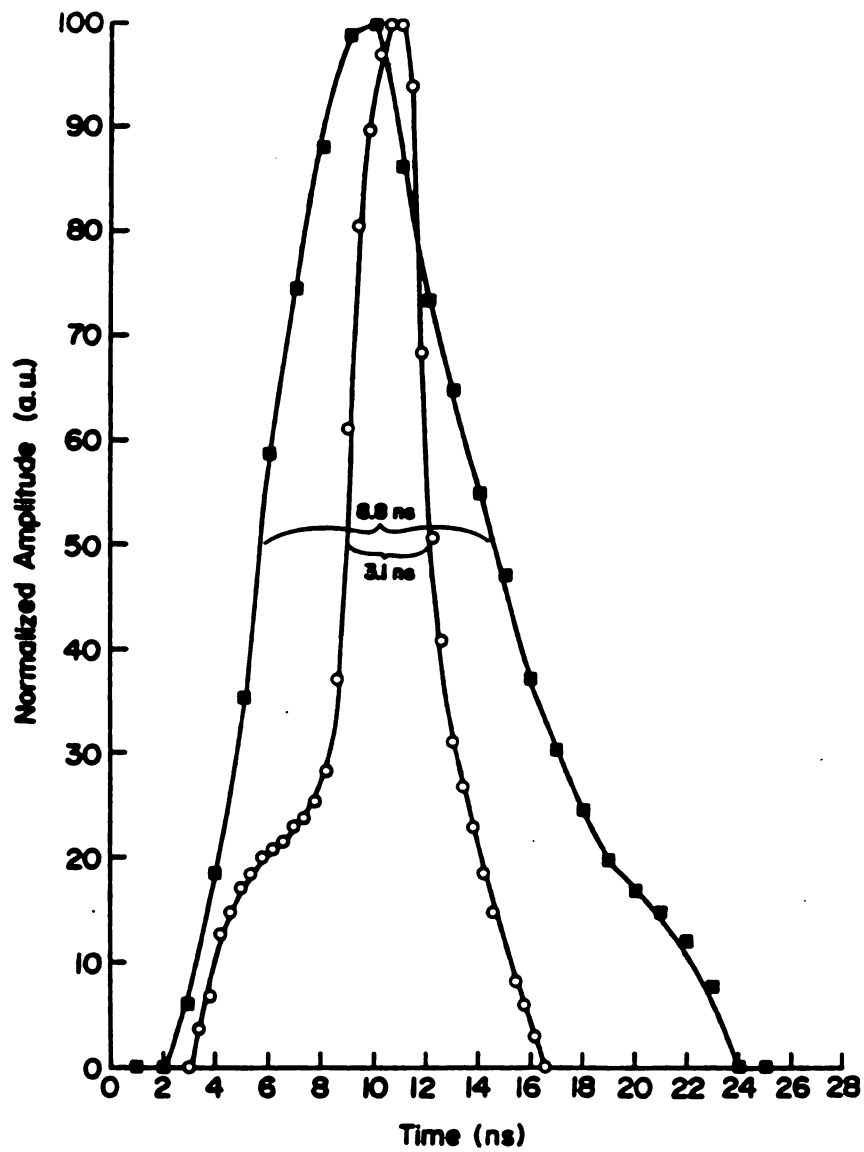


Figure 2-4. Temporal overlap and pulse shapes of the N₂ (■) and dye (○) lasers.

followed by precision flowmeters (Series FM-1050, Matheson Instruments, Horsham, PA). These flowmeters were roughly calibrated by connecting the burner head to a paddle-type flowmeter (Model 1755, Rockwell Manufacturing Co., Anaheim, CA) with a 3.2 cm id rubber hose. A stopwatch was used to determine the amount of time necessary to collect either 0.5 or 1.0 L of gas at a particular setting. Typical data are shown in Figure 2-5 for the mantle flame. It should be noted that any changes in the flow system, such as changes in nebulizer adjustment, will change the calibration. In general the central and mantle Ar settings used gave a flow of approximately 3.2 L/min. The mantle flame H_2 and O_2 flow settings gave a stoichiometric mix of 1 L/min and 0.5 L/min respectively. The central flame H_2 and O_2 settings were adjusted to give maximum DLI signals. These occurred under slightly fuel-rich conditions.

The original nebulizer used was based on a design of Donohue and Carter⁹⁶ and has been described elsewhere⁹⁷. The only major modification was in the use of stainless steel, rather than glass, capillaries. The glass needles were easily broken and difficult to reproduce and replace. To manufacture the stainless steel capillaries, a small bead of silver solder was placed on the tip of a 2 mm outer diameter stainless steel tube. A small hole was then drilled through the center of this bead and finally the bead was turned to a conical point.

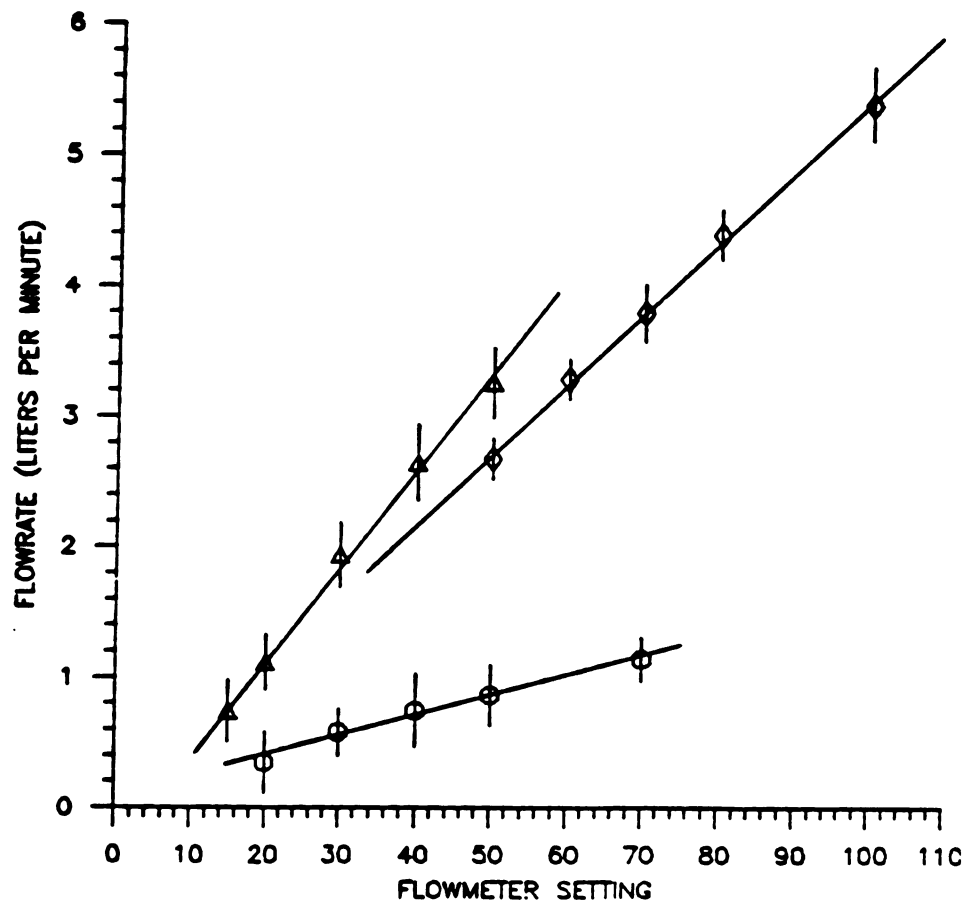


Figure 2-5. Mantle flame flowmeter calibration data ($\diamond$) Ar; (Δ) H₂; ($\circ$) O₂.

Satisfactory flow rates were obtained with a 0.025 inch hole for the solution uptake capillary and a 0.026 inch hole for the crossed-flow capillary. These capillaries were found to be virtually indestructible over hundreds of hours of use. Even so, this nebulizer design displayed instabilities as the capillary sleeves could slip in their fittings and change the capillary positioning. To alleviate this problem a new nebulizer was designed (with the help of C.A. van Dijk). In this design, shown in Figure 2-6, the nebulizer body was expanded. This allowed the capillaries to be set into sleeves which could be screwed into tapped holes in the nebulizer body. The cross-flow capillary sleeve was inset in the body and the Ar brought in through another fitting (also set in a tapped hole). Once set, the capillary could not be moved by jarring the nebulizer. The solution uptake capillary was strapped to the nebulizer body to prevent movement. This arrangement proved to be very reliable.

For the analytical applications described in Chapter VI, an air-acetylene flame was used. This flame is described in Chapter VI.

D. Signal Detection and Processing

D-1. Ionization Signals

Several collection circuits were tried before a final design was chosen. This design is shown in Figure 2-7. The configuration of the amplifier is a

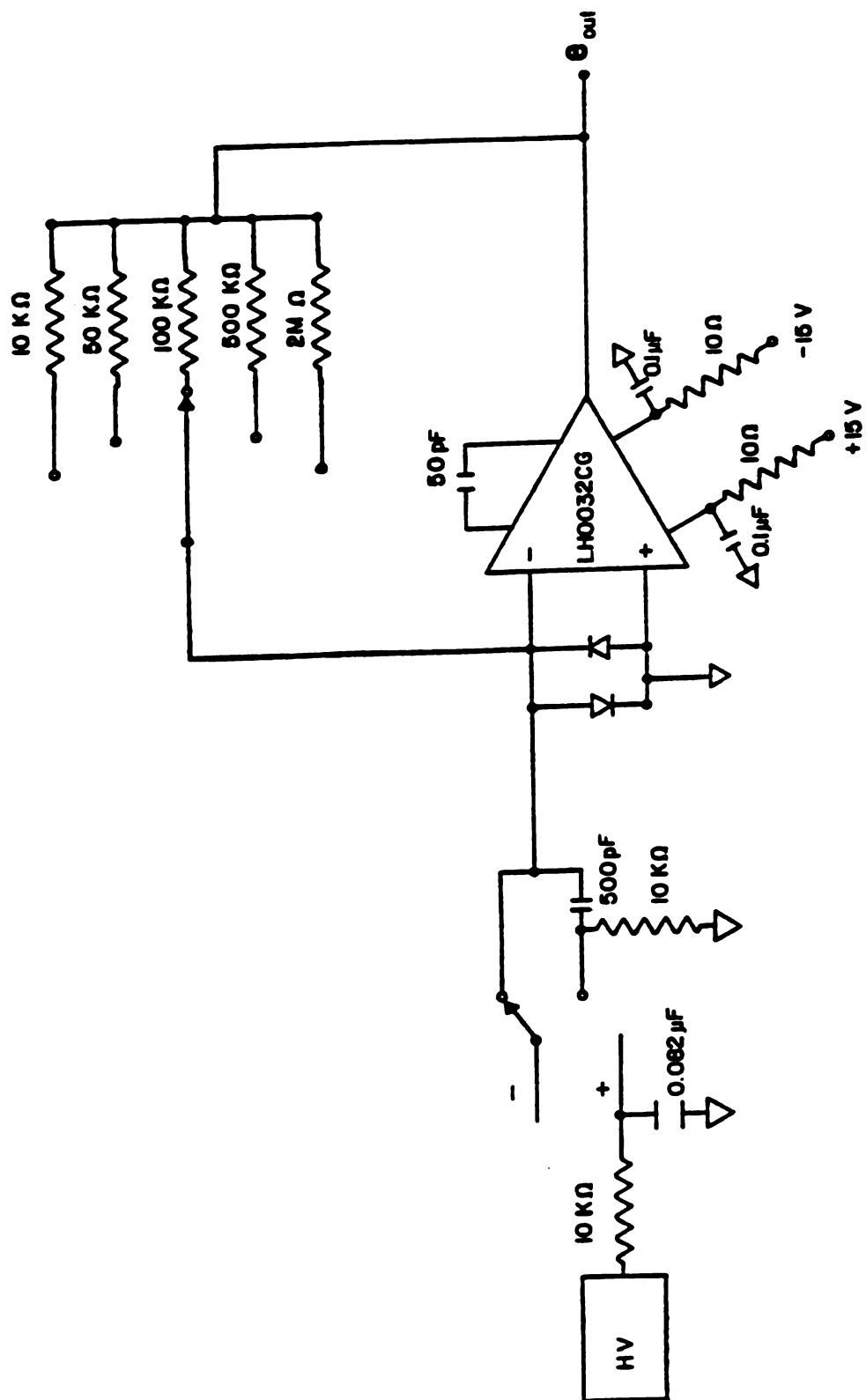


Figure 2-7. Ionization signal collection circuitry.

modification of a circuit described by Havrilla and Green⁹⁸.

The probes used to collect the ionization signal were either iridium or nichrome in composition. The former were found to be less susceptible to contamination, but the latter were much less expensive and experimentally acceptable as long as they were cleaned (sanded) or replaced frequently. The anode was held in place with a banana jack set into a translation stage attached to the burner head mount. The cathode was soldered into a quick-connect spade bit whose mate was also clamped to a translation stage set on the burner head mount. In this manner each probe could be easily replaced and could be moved in three dimensions. In almost all cases the probe diameter was 0.025" (0.64 mm). The probes were connected to the collection circuit with a subminiature BNC cable (RG-174, Amphenol North American, Oak Brook, IL) which was chosen both to provide shielding and to minimize stray capacitance. For the same reasons the leads were kept as short as possible. To reduce RFI pickup further, the cables were inserted into shielding braid which was connected by solder to the miniature BNC connector which, in turn, was grounded to the case. Also, the connectors at the probe ends were insulated with tissue paper and then wrapped by aluminum foil which was in turn strapped to the shielding braid. These measures

left only the actual probes unshielded and reduced RFI significantly.

The operational amplifier used was an "Ultra Fast" JFET amplifier (LH0032CG, National Semiconductor, Santa Clara, CA). The slew rate for this amplifier is 500 V/ μ s, and it has a 70 MHz bandwidth. The amplifier circuit is contained in a grounded aluminum case. The grounding was accomplished by attaching it to the burner head mount. This also helped to minimize the length of the probe cables. All connections, including amplifier supply voltage and high voltage, were made by BNC connectors as the use of banana cable was found to increase the RFI pickup dramatically. The supply voltage (± 15 V) was obtained from a commercial power supply (AD902, Analog Devices, Norwood, MA) in a home-made circuit set in a shielded case. The probes were biased by a high voltage power supply (Model 3K10B, Power Designs, Inc., Westbury, NY).

As shown in Figure 2-7, a single pole double throw (SPDT) switch on the input allows the ionization signal either to go directly to the amplifier or to pass through a high pass filter network. In the former configuration the circuit acts simply as a current-to-voltage converter. The gain was made switch selectable with nominal values of 10^4 , 5×10^4 , 10^5 , 5×10^5 and 2×10^6 V/A (with feedback resistors of 10, 50, 100, 500 and 2000 k Ω , respectively). In the other configuration

the gain is frequency dependent as the input capacitor, the operational amplifier and the feedback resistor act together as an active high pass filter, and the 10 k Ω resistor acts simply as a load. The frequency response curves for each of the configurations were obtained experimentally and are shown in Figure 2-8. To obtain these, sine waves of varying frequencies were fed to the input through a 10 k Ω resistor. The amplitude was held constant at 0.01 V peak-to-peak so the input signal variations were 1 μ A (about the same as a typical ionization signal). The output amplitude was observed to measure the gain. In both the current amplifier (Figure 2-8a) and filter (Figure 2-8b) configurations the response is seen to roll off at high frequencies. This is due to bandwidth limitations of the circuit. In the filter configuration low frequency signals (≤ 1 kHz) are strongly attenuated.

The filter was found to have little effect in experiments involving the H₂-O₂-Ar flame, but was essential for the elimination of low frequency flame noise when the air-acetylene flame was used. In typical experiments either the 100 or 500 k Ω feedback resistor was used.

The output of this circuit was processed by a boxcar integrator that has been described elsewhere¹⁸. In typical experiments the ionization signal was observed to be on the microsecond (μ s) time scale (see Section A). Because of this, a 5 μ s aperture (gate width) with a 50 μ s aperture delay range was normally employed. The

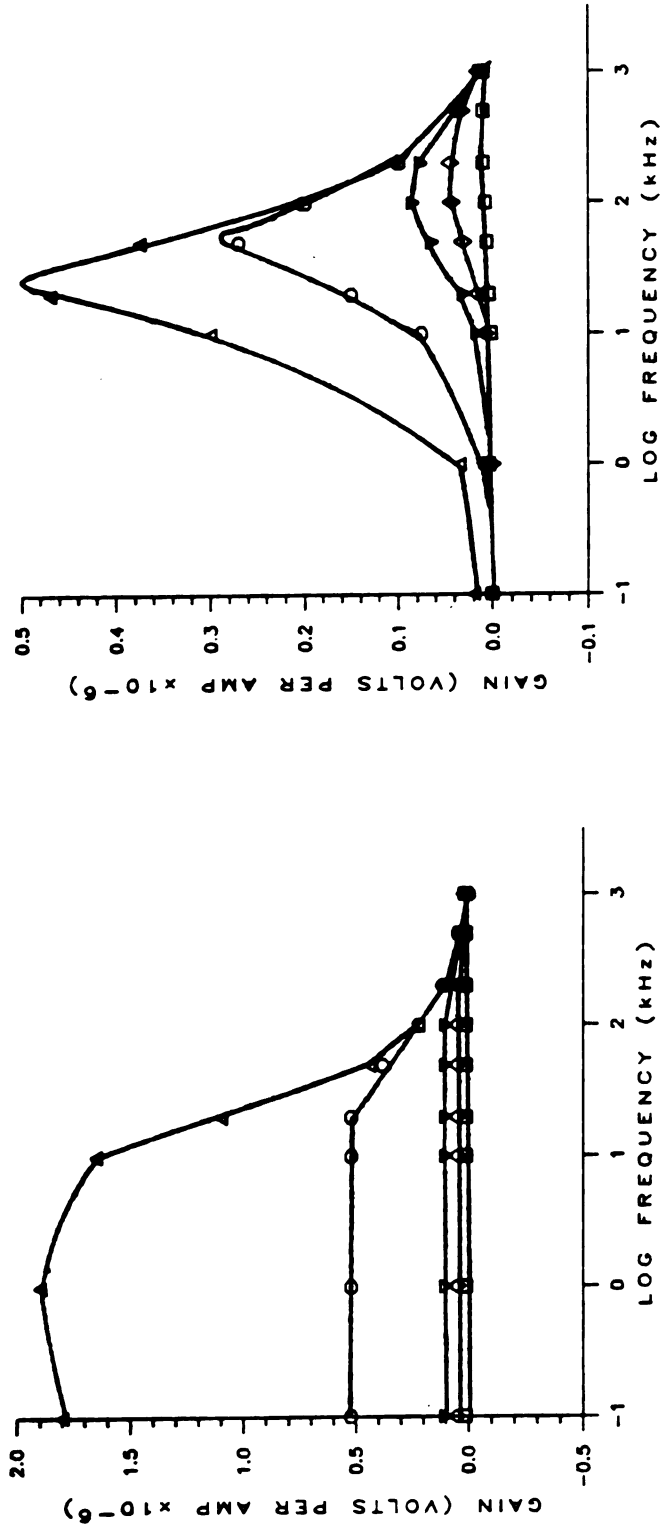


Figure 2-8. Frequency response of the ionization collection circuit for (a) current amplifier configuration and (b) filter configuration. (Δ) 2 M Ω feedback resistor; ($\bigcirc$) 500 k Ω feedback resistor; (∇) 100 k Ω feedback resistor; ($\diamond$) 50 k Ω feedback resistor; ($\square$) 10 k Ω feedback resistor.

percent delay was varied from experiment to experiment to achieve the best possible S/N ratios in each case, but values from 6.8 to 7.8% were common. The boxcar was triggered by a 20 volt, 20 ns pulse obtained from an output on the N₂ laser. This pulse occurred when the laser fired, but a small modification in the circuit was necessary as the resistors used by the manufacturer were not rated for the voltages used. These were replaced. Best results were obtained when triggering on the negative edge of the pulse. In all experiments the exponential averaging mode was used and usually the input was AC coupled. Typical input and output time constants were 10 μ s and 0.1 sec, respectively.

The output of the boxcar integrator was the input either to a strip chart recorder for data reduction by hand or to a microprocessor for further processing¹⁹.

D-2. Optical Signals

The optical system used for fluorescence detection has been described by Lin¹⁸. Briefly, a grating monochromator (either Model EU700 or Model EU700-56, GCA/McPherson, Acton, MA) was used for wavelength isolation. This was followed by a photomultiplier module (Model EU701-30, GCA/McPherson, Acton, MA) which housed either a 1P28 or a 1P28A photomultiplier tube (RCA, Inc., Beltsville, MA). The PMT was wired for fast pulse detection as recommended by the manufacturer⁹⁹. The DC output of

this module was the input to one of two current amplifiers. For most studies a homebuilt current amplifier, based on the design of Christmann¹⁰⁰, was used. To improve the input circuit of this design, a precision, low power, FET electrometer amplifier (Model AD515JH, Analogue Devices, Norwood, MA) was used. The bandwidth of this system did not allow study of undistorted fast fluorescence signals and so was used when signal magnitude only was important. For undistorted signals a circuit based on a wide bandwidth linear amplifier (Model CA2812, TRW, Inc., Lawndale, CA) was used. The instantaneous bandwidth of this amplifier is 1 to 520 MHz, and the rated gain is 30 dB (this represents a linear gain of 25). The amplifier output was either integrated by the boxcar or displayed on an oscilloscope. When the boxcar was used a delay line was necessary as prompt fluorescence decays on the nanosecond time scale and there is a minimum gate delay of 75 ns associated with the boxcar triggering electronics. For this, a 75' length of BNC cable was used to carry the signal. In all cases the monochromator was situated at a 90° angle to the dye laser beam; in most cases a lens was used to focus fluorescence onto the entrance slit.

For laser wavelength calibrations and bandwidth studies the same optical system was used (procedure given in Section B). In these experiments the laser

beam was directed to the entrance slit with either a mirror or a quartz flat placed on the burner head.

For thermal emission measurements the slower current amplifier was always used with display on the stripchart recorder.

To observe the temporal characteristics of the laser pulses a fast PIN photodiode (Model 4220, Hewlett Packard, Palo Alto, CA) was used. The circuit for this is shown in Figure 2-9. In this circuit the load resistance was made switch-selectable so that a wide range of light intensities could be observed. In experimental situations the lower values were used if possible because these produced the least amount of signal distortion. The output of this circuit was displayed on a storage oscilloscope (described in Section B).

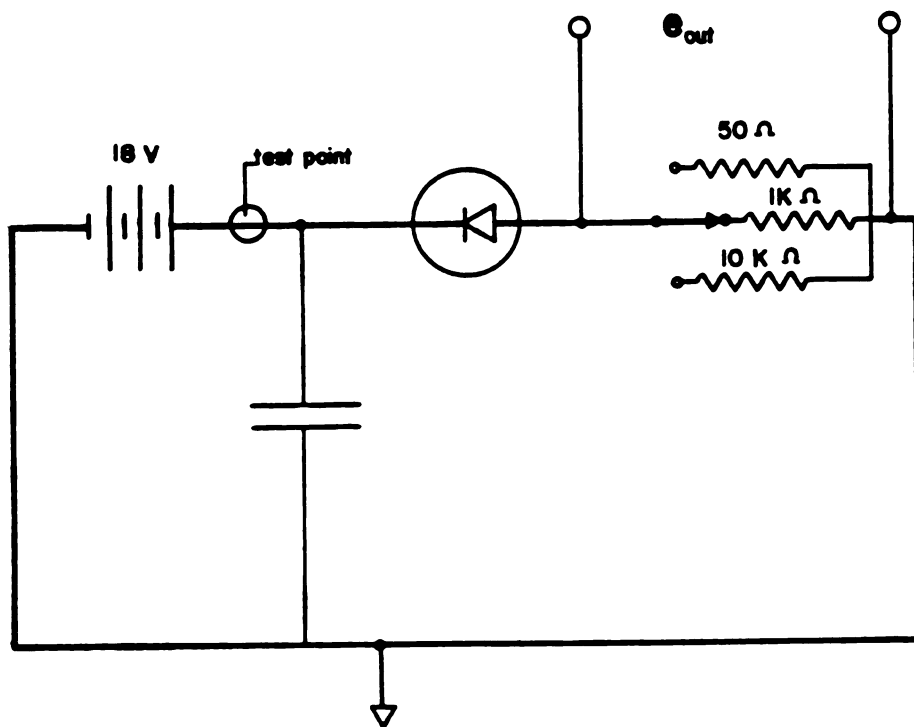


Figure 2-9. PIN photodiode circuitry.

CHAPTER III

ENERGETIC CONSIDERATIONS IN DUAL LASER IONIZATION*

A. Introduction

As noted in the first chapter, laser-enhanced ionization (LEI) has proven particularly useful in the analysis of trace metals in flames. Briefly, a laser is used to excite selectively a resonance of an analyte contained in a flame. This decreases the energy necessary for collisional ionization, and the resultant increase in ionization is detected opto-galvanically. DLI is a closely related technique that has also shown promise in trace metal analysis^{15,16}. The technique permits non-photometric flame temperature determinations¹⁷. In DLI a second laser is used to ionize the analyte from its dye laser excited level. Under the proper experimental conditions the DLI signal can be orders of magnitude greater than LEI signals obtained with dye laser excitation alone. To achieve such enhancements, it is necessary to choose an excitation scheme in which photoionization from the excited state dominates collisional ionization.

In this chapter, a review of applicable theory is used to elucidate the efficacy-determining aspects of DLI

ionization schemes exemplified in experiments with Li, Na, K, Ca, Sr, In and Cs. The widely varying enhancements in DLI signals over LEI signals are traced to their quantum mechanical source.

B. Experimental

B-1. Apparatus

The experimental system used in these studies has been completely described in Chapter II. The laser dyes used and typical laser powers are listed in Table 3-1.

B-2. Reagents

Most solutions were prepared from reagent grade chemicals dissolved in distilled, deionized water. The chloride salts of Na, Li, K and Ca were used as was the bromide salt of Cs and the nitrate salt of Sr. A commercial atomic absorption standard (Aldrich Chemical Co., Inc., Milwaukee, WI) was diluted for use in the experiments involving In.

B-3. Charge Sheath Avoidance

Charge sheath formation about the cathode has been observed in both DLI¹⁶ and LEI^{13,69-71} experiments. These sheaths result in reduced ion collection efficiencies at high analyte concentrations. Care was taken in this study to use analyte concentrations which produced negligible charge sheathing effects as actual signal magnitudes were to be compared and thus collection circuit-limited signals were to be avoided.

TABLE 3-1. Laser Characteristics

A. Excitation beam-Hänsch design, nitrogen-pumped dye laser

Typical Peak Power at Analytical Line — 5 kW

<u>Laser Dye</u>	<u>Approximate Wavelength range (nm)</u>
PBB0 ^a	395 - 410
Stilbene 420 ^a	410 - 440
Coumarin 460 ^a	450 - 480
Rhodamine 6G ^b	565 - 605
DCM ^a	630 - 710

B. Ionizing beam — Nitrogen Laser (Model 0.5-150, NRG, Inc., Madison, WI)

Typical Power in Ionizing Beam — 100 kW

Wavelength — 337.1 nm ($29,665\text{ cm}^{-1}$)

^aDyes obtained from Exciton Chemical Co., Inc., Dayton, OH.

^bDye obtained from Eastman Kodak Co., Rochester, NY.

C. Ionization Mechanisms

Ionization pathways common to laser atomic spectroscopy in flames are shown in Figure 3-1. These can be grouped into two general classes: laser-assisted collisional ionization and direct photoionization. Schemes A-D fall into the first class and have been explored in the laser-enhanced ionization experiments performed to date. Scheme E is of principal interest in DLI. A brief description of collisional processes in flames precedes consideration of the laser ionization schemes.

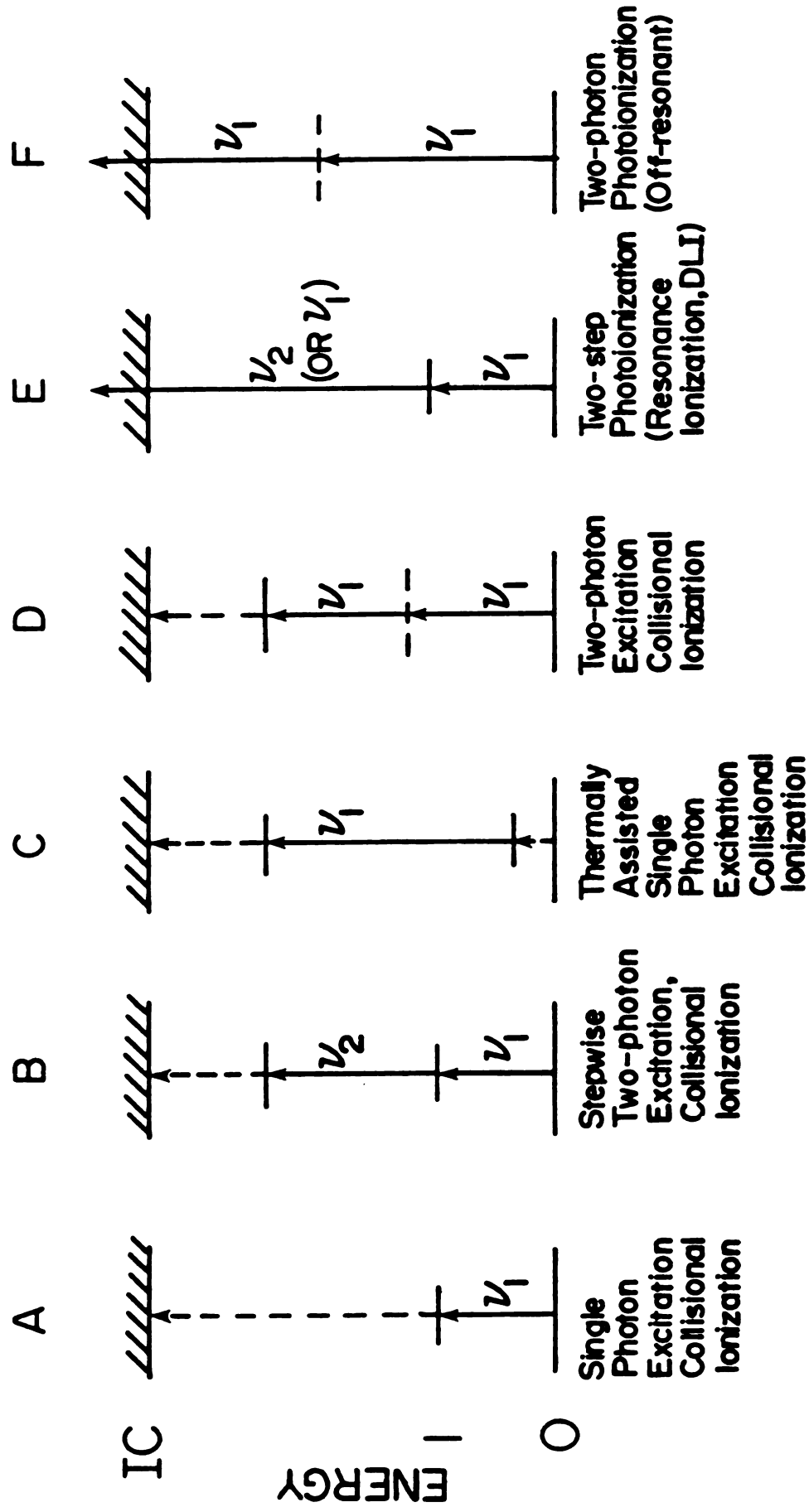
The rate constant for collisional ionization from a given analyte energy level, ℓ , in a flame has been developed by Lawton and Weinburg¹⁰¹ and can be expressed as

$$k_{i\ell}^c = n_x \left[\frac{8kT}{\mu\pi} \right]^{\frac{1}{2}} Q_{x\ell}^c \exp \left[-\frac{(E_i - E_\ell)}{kT} \right], \quad (1)$$

under the assumption that the reduced mass of the collision pair, μ , can represent an average over all collision partners. In Equation III-1, n_x is the number density of the collision partner and this is assumed to be constant here and in following chapters. This makes the collisional rate equations pseudo first-order. Also, T is the flame temperature, $Q_{x\ell}^c$ is the partner-averaged cross-section for collisional ionization from level ℓ , the term $(E_i - E_\ell)$ is the energy difference between the ionization continuum and the level ℓ (hereafter referred to as the energy defect, ΔE), and other symbols take on their usual meanings. If charge

Figure 3-1. Common ionization pathways in laser atomic spectroscopy.

Laser-Assisted Ionization Mechanisms



recombination is negligible, the total rate of ionization of a specific species in the flame can be expressed as:

$$\frac{dn_i}{dt} = \sum_j k_{ij}^c n_j, \quad (2)$$

where k_{ij}^c is the rate constant for the production of ions from level j and n_j is the number density of level j .

In the absence of any optical input, if a Boltzmann distribution of level populations is assumed, it may be seen that there are two competing exponentials involved in the ionization process. Ionization from high-lying levels is exponentially favored as the energy defect is decreased. The number density of these states, however, decreases exponentially with the state energy. If a strong optical field, e.g. that produced by an organic dye laser, is tuned to a resonant transition of the analyte which terminates in state ℓ , such that for all levels $j \neq \ell$, $|k_{ij}^c n_j| \ll |k_{i\ell}^c n_\ell|$, then Equation 2 can be reduced to

$$\frac{dn_i}{dt} = k_{i\ell}^c n_\ell. \quad (3)$$

This is the "opto-galvanic" effect as it applies to the LEI experiment. Scheme A in Figure 3-1 shows this in its most basic (and earliest-implemented) mechanisms. A dye laser is tuned to promote the analyte to an excited real atomic level, from which it is collisionally ionized. Scheme B shows a similar mechanism, but here a second dye

laser is tuned to another transition, thus producing stepwise excitation which further decreases the energy defect; this has been shown to increase the collisional efficiency substantially^{9,13,76,77,79}. The scheme is used most effectively to increase sensitivity for atoms with high ionization potentials. The mechanism in C is commonly termed non-resonant LEI because the lower state of the laser-induced transition is not the ground state of the analyte, but rather a collisionally populated level. The fourth scheme (D) shows a seldom-used variation of the LEI technique. This is multi-photon excitation through a virtual atomic level, in which the dye laser is tuned so that two dye photons match the energy necessary for a one-photon forbidden transition. This is a special case of Scheme B and high-lying excited states can be reached; however, cross-sections for two-photon absorption are generally very low unless the necessary photon energy is very near a real atomic level. As would be expected in an LEI experiment, sensitivity is very much dependent on the choice of transition. Good candidates will have sufficiently high oscillator strengths to permit saturation with obtainable dye laser power.

The final two ionization pathways shown (schemes E and F) involve direct photoionization. In the first, the absorption of a resonant photon is followed by photoionization via absorption of a second photon of

energy greater than or equal to the energy defect. Here the rate constant for photoionization from the laser-excited level, ℓ , is given by

$$k_{i\ell}^p = Q_{i\ell}^p \Phi \quad (4)$$

where $Q_{i\ell}^p$ represents the cross-section for the absorption of an ionizing photon by an atom in state ℓ and Φ is the photon flux of the ionizing beam. Obviously, in any resonance ionization experiment in a flame, such as DLI, the collisional contributions cannot be eliminated and the total rate of ionization from the laser-excited level, ℓ , is given by:

$$\frac{dn_i}{dt} = \left(k_{i\ell}^p + k_{i\ell}^c \right) n_{\ell} \quad (5)$$

Conditions can be chosen, however, under which photoionization will dominate. The final scheme shows purely "off-resonant" photoionization; i.e., direct photoionization without the presence of a resonant intermediate level. This may contribute background ionization in the DLI experiment (see Chapter IV).

D. Results and Discussion

The results of the experiments performed in this study are collected in Table 3-2 and will be referred to throughout this section. The table lists in each row the analyte and resonance excitation wavelengths involved, the energy gap between the excited state and the ionization

Table 3-2. Collection of numerical results and useful spectroscopic data.

Element & excited transition	Dye Laser wavelength (nm)	Energy of excited state ^a cm ⁻¹	Oscillator strength of resonant transition ^c	Transition probability ^c (10 ⁸ /sec)	Ionization Potential cm ⁻¹	Energy Defect (ΔE) cm ⁻¹	Energy Over- shoot (E _{os}) eV ^b	Enhancement Factor ^d
Li(2s+2p)	670.7	14904	0.502	0.372	43487	28583	1082	10 ³
Na(5s+3p)	589.0	1973	0.647	0.655	41450	24477	5188	10 ²
Ca(4s+4p)	422.7	23652	1.75	2.18	49305	25653	4012	10 ²
Sr(5s+5p)	460.7	21698	2.01	1.92	45926	24228	5437	10 ²
In(5p+6s)	410.1	24373	0.14	0.56	46670	22297	7368	1.4
K(4s+5p)	404.4	24720	6.1x10 ⁻⁵	0.0124	35010	10290	19375	1
Cs(6s+7p)	455.5	21947	0.0117	0.0188	31407	9460	20205	1
Na(5p+5s)	616.1	33201	0.059	0.052	41450	8249	21416	1
Ca(3d+7p)	424.0	45425	---	---	49305	3880	25785	1
Li(2s+3d)	639.2	31283	---	---	43487	12204	17461	1
Na(3s+4d)	578.7	34549	---	---	41450	6901	22764	1

^aEnergies in wavenumbers obtained from Moore, C. E. "Atomic Energy Levels", Circular of the National Bureau of Standards 467, U.S. Government Printing Office: Washington, D. C., Vol. 1 (1949), Vol. 11 (1952) and Vol. III (1958).

^bEnergies in electron volts calculated from wavenumber data and rounded to two decimal places.

^cData taken from Reader, J.; Corliss, C. H.; Wiese, W. L., Martin, G. A. "Wavelengths and Transition Probabilities for Atoms and Atomic Ions", NSRDS-NBS, Government Printing Office: Washington, D. C., 1980.

^dSee text for explanation of enhancement factors.

continuum (i.e. the energy defect, ΔE), the energy in excess of this gap provided by the N_2 laser (i.e. the energy of overshoot, E_{os}) and the DLI enhancement factor at the laser powers stated in Table 3-1. The enhancement factor is the ratio of the ionization signal obtained with and without the N_2 laser present.

Before the results are described in detail, some background information about the nature of these enhancement factors must be provided as they are not meant to be absolute measurements. In the cases to be presented in which photoionization is the dominant mechanism of signal production, the resonant transition was found to be saturated by the dye laser system. Results of these experiments are presented elsewhere (see Chapter IV); it suffices here to note that at the focal point of the dye laser, the power density was at least one order of magnitude greater than the experimentally determined threshold for saturation. In cases where DLI enhancement was observed, the signal depended linearly on the ionizing (N_2) beam power. In the experimental apparatus used, the N_2 laser beam was brought to a tighter focus than was the dye laser beam. Hence the LEI signal emanated from a larger region of the flame than did the DLI signal in every individual experiment. Somewhat different flame volumes were irradiated by the 670.7 nm and 589.0 nm dye laser beams in the Li and Na experiments, whereas the N_2

laser irradiated the same volume. Thus the enhancement ratios are not perfectly comparable. In addition, no correction for possible variations in nitrogen laser power have been made. Thus the enhancement ratios are presented as simple orders of magnitude.

At constant analyte concentration, the LEI signal can be increased only by increasing the saturated irradiated volume, but the DLI signal can be increased by increasing either the power density in the ionizing beam or the area of overlap at constant power density. Thus, the enhancement factors quoted refer to those generated by the available laser system, not to the maximum fundamental enhancement factors possible.

As the data of Table 3-2 show, four experiments were performed in which a significant enhancement factor was obtained. In each of these experiments it can be seen that the match between the N_2 laser photon energy (3.68 eV) and the energy defect is within 0.7 eV. For example, an enhancement factor of 100 was found with Na as the analyte and the dye laser tuned to the Na D line at 589.0 nm, $Na(3S_{1/2} \rightarrow 3P_{3/2})$. Here the overshoot energy, E_{OS} , is moderate (0.64 eV) and the oscillator strength of the resonance transition is reasonably large (0.647).

It should be noted that the $Na(3S_{1/2} \rightarrow 3P_{1/2})$ transition produced a similar enhancement factor. In all cases where spectrally resolvable multiplets were available, the strongest line was used. It is also worth mentioning that

oscillator strengths, although noted herein, are essentially irrelevant to the analysis of the DLI vs. LEI enhancement; ionization from a truly saturated excited state should be independent of the ease or difficulty of the state's saturation.

Similar DLI flame experiments involving Ca, Sr, and Li were performed with analogous results. The Ca(4s $\rightarrow$ 4p) and Sr(5s $\rightarrow$ 5p) transitions, occurring at 422.7 and 460.7 nm respectively, possess large oscillator strengths and have energy defects almost equal in size to that found in Na. In both cases the enhancement factor is found to be of the order of 100. The enhancement factor found with the dye laser tuned to the Li(2s $\rightarrow$ 2p) transition was the largest of any studied. The energy defect is larger in this case than in the others and this implies both a decrease in collisional ionization efficiency and a better energy match in the photoionization process (i.e. small E_{OS}), since the ionizing laser frequency was unchanged. These factors will be discussed in more detail below.

As an example of the differences in signal obtained with and without the ionizing beam, the results of a typical study (with Li as the analyte) are presented in Figure 3-2. In this experiment, the sample was nebulized into the flame and the dye laser scanned across the Li(2s $\rightarrow$ 2p) transition. In the figure, the ionization signal is plotted versus wavelength for the DLI (upper

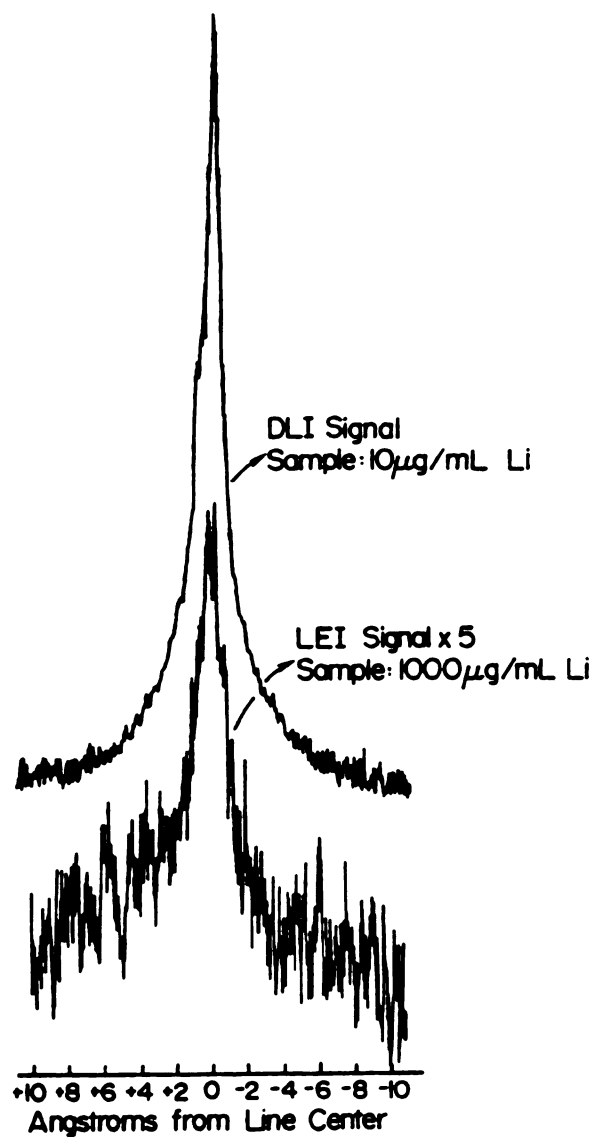


Figure 3-2. Ionization signal versus wavelength for DLI (upper trace) and LEI (lower trace). Dye laser scanned across the $\text{Li}(2s \rightarrow 2p)$ transition at 670.7 nm. To obtain the LEI signal, the sensitivity (vertical scale) was increased by a factor of 5 and the analyte concentration by a factor of 100.

trace) and the LEI (lower trace) cases. To obtain the LEI signal, the measurement sensitivity was increased by a factor of 5 and the Li concentration was increased by a factor of 100, as indicated in the figure.

The DLI experiment was attempted with In as the analyte, with the In(5p $\rightarrow$ 6s) transition at 410.1 nm in resonance. Only a small enhancement factor was obtained.

Non-resonant transitions were used in experiments with both Na and Ca. In both cases the ionization signal was derived strictly from the LEI process (Scheme C). With Na, the dye laser was tuned to excite the Na(3p $\rightarrow$ 5s) resonance at 616.1 nm; the 3p level was thermally populated. Here, the energy defect after the one-photon absorption step was quite small (1.03 eV) and consequently the E_{os} value was very large compared to those cases in which enhancements were observed.

Two-photon excitation involving the Na(3s $\rightarrow$ 4d) transition at 578.7 nm and the Li(2s $\rightarrow$ 3d) transition at 639.2 nm were also examined (Scheme D). As in the case of the non-resonant transitions described above for Na and Ca, these transitions populated electronic states with such small energy defects that no signal enhancement was observed upon addition of the ionizing laser beam.

Finally, resonant transitions in both Cs and K were studied. In both the case of the Cs(6s $\rightarrow$ 7p) transition at 455.5 nm and the K(4s $\rightarrow$ 5p) transition at 404.4 nm, resonant LEI only was found (Scheme A). Once again, no

signal enhancement occurred when the N_2 beam was added. Indeed, some direct two-photon ionization (Scheme F) was observed at high concentrations of Cs and K with the N_2 beam alone. If the latter mechanism contributes at the lower concentrations used in the experiments reported in Table 3-2, decreased signal-to-noise ratios would result with the N_2 beam present because this source of background ionization should fluctuate dramatically with fluctuations in the N_2 laser power due to the squared power dependence.

Intrepetation of the foregoing results requires consideration of two features of the ionization process which determine the efficacy of DLI in flames. As discussed below, photoionization cross-sections depend on E_{0s} . In cases of "electrical" saturation^{68,102,103}, the near unit efficiency of collisional ionization from excited states precludes a significant DLI enhancement, moreover, collisional ionization may compete with photoionization for dominance even in the absence of such saturation.

The general (and approximate) result that the ionization cross-section for atoms undergoing photo-absorption decreases with increasing energy overshoot, E_{0s} , has been recognized in various limited cases since at least 1930. As discussed by Heitler¹⁰⁴, this important qualitative feature can be predicted for the photoelectric effect in K-shell atoms, both with the Born approximation,

in which high energy electronic continuum states are represented simply as $\exp(ipr/\hbar)$, and with accurate numerical representations of the continuum electronic wavefunctions near the absorption edge¹⁰⁵. Several model calculations have yielded cross-sections as functions of photoionizing frequencies for light alkali atoms in ground and excited states¹⁰⁶⁻¹¹⁶.

A general decrease in photoionization cross-sections with increasing energies of the "final" electronic continuum states can be termed "hydrogenic" behavior; Bethe and Salpeter demonstrated monotonic cross-section decreases for hydrogen¹¹⁴. The physical principle underlying this behavior can be seen easily. Photoionization cross-sections depend upon the square moduli of radial matrix elements of the form

$$R_{n\ell, \ell'}(\epsilon) = \int_0^\infty r P_{n\ell}(r) P_{\epsilon\ell'}(r) dr, \quad (6)$$

where $P_{n\ell}(r)$ and $P_{\epsilon\ell'}(r)$ are the radial wavefunctions of the valence electron initial and final states. The higher the electronic continuum energy, ϵ , the more oscillatory the continuum electronic wave function $P_{\epsilon\ell'}(r)$ will be, and cancellation may be expected to reduce the radial matrix element and hence the cross-section. In actuality, when both the discrete and continuum states are oscillatory, it is possible that the oscillations may coincide for some ϵ values, thus giving rise to structure in the

photoionization cross-section. For example, the calculated photoionization cross-section for Cs(5d) shows two minima¹¹⁵; more simply, the 4p and 5p cross-sections for K show maxima displaced from the ionization threshold¹¹³. Thus in practical analytical applications, the simplest approach to optimization of the DLI signal is an ionization scheme which minimizes E_{OS} . It should, however, be recognized that photoionization cross-sections may possess structure and thus permit additional optimization.

The competition of collisional and photo-absorption routes to ionization enters the interpretation of the DLI experimental results reported above. The analysis is aided substantially by consideration of various theoretical^{107,108,110,113,114} and experimental^{117,118} cross-sections for these processes given in the literature. The discussion that follows employs comparisons of DLI enhancements ratios, and the caveats presented in the previous section are applicable.

The largest enhancement ratio reported in Table 3-2 is that for Li ($2s \rightarrow 2p \rightarrow IC$). It is instructive to compare the three order of magnitude enhancement realized in the Li experiment with the factor of 100 achieved with Na($3s \rightarrow 3p \rightarrow IC$). (In both cases the excited states were observed to be saturated). There exist both experimental¹¹⁷ and theoretical¹¹³ results suggesting a Na($3p \rightarrow IC$) photoionization cross-section of approximately 4 Mbarns at the N_2 laser wavelength. Similar experimental¹¹⁸ and

theoretical¹¹³ results for $\text{Li}(2p \rightarrow 1s)$ indicate an approximate cross-section of 17 Mbarns at 337.1 nm. The ratio of these cross-sections is consistent with the ratio of observed DLI enhancements; moreover, consideration of the relative collisional ionization cross-sections suggests a larger relative enhancement for Li than that predicted simply by the ratio of photoionization cross-sections. Kelley and Padley¹¹⁹ have calculated the average collisional cross-sections for a thermal population (2100-2800 K) of Na and Li atoms in collision with Ar and H_2O , the principal collisional partners in the flame under study. The values $\sigma_{\text{Na},\text{H}_2\text{O}} = 11,000 \text{ \AA}^2$, $\sigma_{\text{Na},\text{Ar}} = 2700 \text{ \AA}^2$, $\sigma_{\text{Li},\text{H}_2\text{O}} = 3500 \text{ \AA}^2$, and $\sigma_{\text{Li},\text{Ar}} = 1200 \text{ \AA}^2$ may be considered approximations to the corresponding cross-sections specific to the Na 3p and Li 2p states. If collisional ionization is more probable in Na after dye laser excitation than in Li, then the DLI to LEI ratio for Na will be smaller than for Li.

Inspection of the results obtained with the dye laser tuned to the Na(3p) and Na(5s) transitions illustrates the potential value of optimization of the ionizing beam energetics and also helps to explain the remainder of the results shown in Table 3-2. For the Na(3p) case the photoionization dominates collisional ionization by two orders of magnitude and the cross-section for absorption of the N_2 beam, referred to previously, is 4 Mbarns. For Na(5s) at the 337.1 nm excitation wavelength the cross-

section is approximately $0.005 \text{ Mbarns}^{116}$ and hence the photoionization contribution to the rate would be significantly smaller. Even if the energy of the ionizing beam were selected to optimize photoionization (the ionization cross-section at threshold from $\text{Na}(5s)$ is 2.7 Mbarns^{116}), collisional contributions would be expected to dominate ionization from $\text{Na}(5s)$. With the conservative assumption that the collisional cross-section is unaffected by excitation, the ratio of the collisional ionization rate constants can be approximated by the ratio of Arrhenius factors from Equation III-1,

$$\frac{k_{5s}^c}{k_{3p}^c} = \exp\left(\frac{\Delta E_{3p} - \Delta E_{5s}}{kT}\right),$$

which in this case is approximately equal to 66,500. Thus the collisional ionization from the $5s$ state would be roughly two orders of magnitude greater than the rate of photoionization. Indeed it has been suggested that the efficiency of collisional ionization from high-lying excited states is near unity¹⁰³. This would represent the "electrical" saturation discussed previously. The validity of the argument presented above is borne out in results of experiments in which Li and Na were used as analytes. Both Zorov, et al.⁷⁶ and Matveev, et al.⁷⁵ attempted three-photon photoionization of Li in a flame. In these experiments two dye lasers, pumped by a single Nd:YAG laser, provided sequential (stepwise) excitation

of Li to the 3d state ($\Delta E = 1.49$ eV). No enhancement in ionization signal was observed when photoionization from this level was attempted with the second harmonic of the Nd:YAG laser ($E_{OS} = 0.84$ eV). Gonchakov, et al.¹⁰ performed a similar study on Na in which the two dye lasers were used to excite Na to its 4d state ($\Delta E = 0.86$ eV) and photoionization was attempted with the Nd:YAG fundamental at $1.06 \mu\text{m}$. The ionizing laser beam was both well matched to the energy defect ($E_{OS} = 0.3$ eV) and powerful, but still no enhancement was observed. On the other hand, photoionization from the 4d level of Na was demonstrated in a study in which the Na was electrothermally atomized in a pure Ar atmosphere at room temperature¹²⁰. Under these conditions collisional ionization is less efficient than in a flame cell, and enhancement was observed upon the addition of the ionizing beam.

The argument above explains why ionization from the K(5p) level, with a photoionization cross-section of about 3 Mbarns, but a ΔE of only 1.28 eV, is predominantly collisional. The same argument might be made in the cases of Ca(7p) and Cs(7p), were the applicable cross-sections available. On the other hand, In(6s) appears to be a good candidate for DLI study with appropriate optimization, although the energy defect is slightly smaller than those in the cases in which significant enhancement was achieved.

Also apparent is the fact that a more versatile DLI system could be easily designed. For example, a Nd:YAG-pumped dye laser system, equipped with a frequency doubling option on the dye laser and frequency doubling, tripling, and quadrupling options for the fundamental, would provide considerable flexibility, especially in the study of high ionization potential elements.

Another natural extension of the DLI technique is its application to more common analytical flames. Preliminary experiments have been carried out with Ca as the analyte in an air-acetylene flame; enhancement factors for this element were similar to those obtained with the H_2-O_2 -Ar flame. Studies on additional elements are in progress.

There are no naturally occurring elements for which the lowest excited state energy defect is less than 1.5 eV, and hence with the exception of a few elements with very high ionization potentials, e.g. rare gases, the majority of the periodic table appears attractive for study. The incorporation of infrared lasers into the DLI technique would be necessary in instances of very low ionization potentials. For example, excitation of Cs to its first excited state requires a photon wavelength of 849 nm. In addition to resonant excitation considerations, appropriate attention to the effect of the ionizing laser wavelength will advance the DLI technique significantly. As new measurements and theoretical calculations of photoionization

cross-sections become available, highly optimized DLI schemes will become easier to design. In the interim, minimization of E_{0s} appears the simplest and most profitable approach to DLI experimental design.

*Obtained jointly with K.C. Lin, G.E. Leroi and P.M. Hunt. P.M. Hunt is particularly acknowledged for his input on the discussion of quantum mechanics.

CHAPTER IV

LASER POWER DEPENDENCE IN DLI AND LEI

A. Introduction

A clear understanding of the effect of laser power on signal generation is necessary for elucidating the fundamental processes involved in laser spectroscopic techniques and for systematically optimizing the methods. In this chapter the effects of laser power on signals obtained in DLI and LEI experiments are examined.

The validity of a "rate equations" approach to systems involving resonant laser excitation has been discussed in the literature^{121,122}. These studies indicate that this approach, rather than the more complex density matrix formulation, can be used as long as no pulsations in the level populations occur at the characteristic Rabi frequency of the system. The experimental system used in this study has been examined by Lin¹⁸ and found to be amenable to the "rate equations" treatment.

Lin also used a three level system to describe DLI processes. Although complete, this system is more complicated than necessary if it can be assumed that ionization processes, both collisional and optical, do not

significantly affect the populations in the dye laser-coupled levels. This assumption allows the use of a simple two level atomic model similar to the one derived for laser excited atomic fluorescence (LEAF) by DeOliveras¹²³. In the next section this type of model is developed. Following this, the validity of the abovementioned assumption is studied. Data from both DLI and LEI experiments are then explained in terms of the model.

B. Theory

A simplified atomic level scheme is shown in Figure 4-1. The rate processes pertinent to DLI are included and labeled a-i. A description of each process is presented below. In this discussion, n_1 , n_2 and n_i are the population densities of the three levels (cm^{-3}), E_d is the spectral irradiance of the dye laser ($\text{W cm}^{-2} \text{ Hz}^{-1}$) and E_i is the photon irradiance of the ionizing beam ($\text{photons cm}^{-2} \text{ s}^{-1}$).

- a) Stimulated excitation rate per unit volume; $n_1 b_{21} E_d$ (B_{12} = Einstein coefficient for stimulated absorption ($\text{cm}^2 \text{ Hz W}^{-1} \text{ s}^{-1}$)).
- b) Stimulated emission rate per unit volume; $n_2 B_{21} E_d$ (B_{21} = Einstein coefficient for stimulated emission ($\text{cm}^2 \text{ Hz W}^{-1} \text{ s}^{-1}$)).
- c) Spontaneous emission rate per unit volume; $n_2 A_{21}$ (A_{21} = Einstein coefficient for spontaneous emission in (sec^{-1})).

- d) Collisional excitation rate per unit volume; $n_1 k_{12}$
(k_{12} = collisional rate constant for the process in which an atom in level 1 is collisionally excited to level 2 (sec^{-1})).
- e) Collisional deexcitation rate per unit volume; $n_2 k_{21}$
(k_{21} = collisional rate constant for the process in which an atom in level 2 is collisionally deexcited to level 1 (sec^{-1})).
- f) Collisional ionization rate per unit volume; $n_2 k_{2i}$
(k_{2i} = collisional ionization rate constant (sec^{-1})).
- g) Photoionization rate per unit volume; $n_2 \sigma E_i$ (σ is the cross-section for absorption of the ionizing laser beam (cm^2)).
- h) Recombination rate per unit volume to the excited state; $n_i k_{i2}$ (k_{i2} is the rate constant for the process in which an ion and an electron combine to produce an atom in excited state 2 (sec^{-1})).
- i) Recombination rate per unit volume to the ground state; $n_i k_{i1}$ (k_{i1} is the rate constant for the process in which an ion and an electron combine to produce an atom in the ground state (sec^{-1})).

This description assumes that multiphoton ionization from the ground and excited levels is negligible as is collisional ionization from level 1. Also, the electron density in the flame is assumed to be constant making the recombination rate equations pseudo first-order. These are reasonable assumptions for most atomic systems in flames.

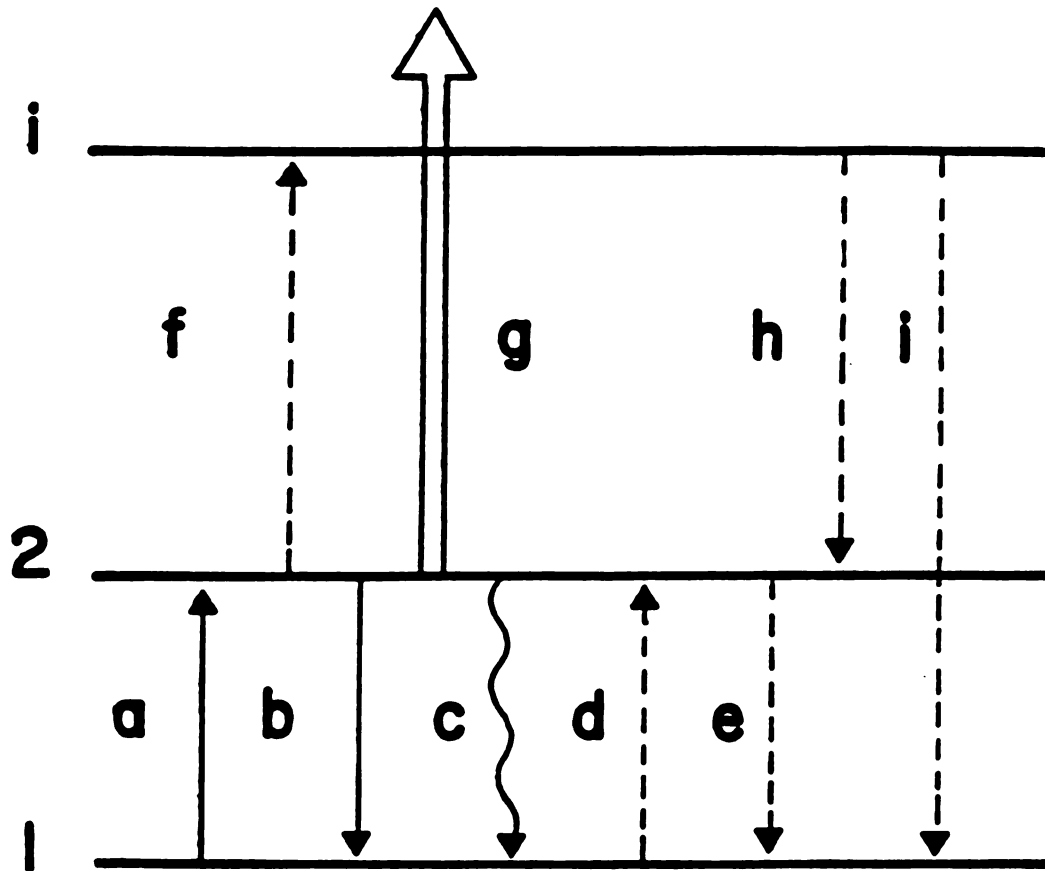


Figure 4-1. Simplified atomic level scheme.

From the above the following rate equations are obtained:

$$\frac{dn_1}{dt} = n_2(B_{21}E_d + A_{21} + k_{21}) - n_1(B_{12}E_d + k_{12}) + n_i k_{i1} \quad (1)$$

$$\begin{aligned} \frac{dn_2}{dt} = & n_1(B_{12}E_d + k_{12}) - n_2(B_{21}E_d + A_{21} + k_{21} + k_{2i} + \sigma E_i) \\ & + n_i k_{i2} \end{aligned} \quad (2)$$

$$\frac{dn_i}{dt} = n_2(k_{2i} + \sigma E_i) - n_i(k_{i2} + k_{i1}) \quad (3)$$

At this point some simplifying assumptions will be made. These are justified for the DLI case under study in the results and discussion section to follow.

Assumptions:

- 1) The photoionization rate in cases where significant DLI enhancement is observed is greater than the collisional ionization rate (i.e. $\sigma E_i \gg k_{2i}$).
- 2) Neither photoionization nor collisional ionization drain the excited state (level 2) to a significant extent (i.e. $B_{21}E_d + A_{21} + k_{21} \gg \sigma E_i + k_{2i}$).
- 3) Collisional excitation is negligible compared to absorption (i.e. $B_{12}E_d \gg k_{12}$).
- 4) Recombination is negligible (this follows from assumption 1) (i.e. $n_i k_{i2} \cong 0$ and $n_i k_{i1} \cong 0$).

with these the rate equations (IV-1)-(IV-3) are reduced to:

$$\frac{dn_1}{dt} = n_2(B_{21}E_d + a) - n_1 B_{12}E_d \quad (4)$$

$$\frac{dn_2}{dt} = n_1 B_{12} E_d - n_2 (B_{21} E_d + a) \quad (5)$$

$$\frac{dn_i}{dt} = n_2 \sigma E_i \cong 0 \quad (6)$$

where the excited state depopulation processes, A_{21} and k_{21} , have been summed into the parameter, a .

These assumptions and rate equations have two important consequences. First, levels 1 and 2 then comprise an isolated system as in the case of resonance fluorescence. Second, the instantaneous ionization signal is an indicator of the excited state population just as resonance fluorescence is.

If levels 1 and 2 are isolated the total atomic population density, n_T , is given by

$$n_T = n_1 + n_2. \quad (7)$$

The two level rate equations approach, taken by DeOliveras, is followed closely in the development here. In the following the dye laser pulse is assumed to be a rectangular (boxcar) function so

$$E_d(t) = \begin{cases} E_0 & 0 \leq t \leq t_0 \\ 0 & t > t_0 \end{cases}$$

where t_0 is the duration of the laser pulse. If Equation (IV-7) is substituted into Equation (IV-5), the rate

equation becomes

$$\frac{dn_2}{dt} = n_T B_{12} E_d - n_2 (a + b E_d) \quad (8)$$

in which b has been substituted for $B_{12} + B_{21}$. Either one of two possible cases will be experimentally encountered. One case occurs if the population in level 2 attains a steady state value (i.e. $dn_2/dt = 0$) and the other if it does not. These cases will be discussed in detail after the nitrogen laser sampling function is examined.

B-1. Ionizing Laser Sampling Function

As a useful first approximation, the nitrogen laser pulse is assumed to be a rectangular function similar to that used to describe the dye laser pulse. Thus the instantaneous ionization signal should be directly proportional to the excited state population just as the instantaneous fluorescence is in laser-excited atomic fluorescence (LEAF). For signal-to-noise enhancement, gated integration is typically used in LEAF and thus the quantity measured is the average fluorescence signal during the gate duration. Similarly, the total ion current measured in DLI is proportional to the average excited state population during the nitrogen laser pulse. One important difference between DLI and LEAF should be noted here. In LEAF with short excitation pulses, very short integrator gate widths must be used because of the short excited state lifetimes of atoms. As discussed

previously (see Chapter II) the ion transit time from the formation region is on the order of microseconds. Thus the boxcar gatewidth can be approximately three orders of magnitude larger in DLI experiments than in LEAF and this simplifies the instrumental approach greatly.

B-2. Steady State Case

If the population in level 2 attains a steady state value, n_2^{ss} , Equation (IV-8) can be solved for n_2 to give

$$n_2^{ss} = n_T \frac{B_{12}}{b} \left(\frac{E_d}{E_d + E_s} \right) \quad (9)$$

where $E_s = a/b$. From Equation (IV-9) it can be seen that, at low irradiances ($E_d \ll E_s$), the excited state population will rise linearly with input laser power. As E_d approaches and surpasses E_s the power dependence becomes nonlinear to a point where complete independence at high spectral irradiances is observed. Since B_{12} and B_{21} are related by

$$g_1 B_{12} = g_2 B_{21} \quad (10)$$

the maximum obtainable value at the saturation limit $n_2^{\max}$, is given by

$$n_2^{\max} = n_T \frac{B_{12}}{b} = n_T \frac{g_2}{g_1 + g_2} \quad (11)$$

Thus the meaning of E_s , the so-called saturation spectral irradiance, is that it is the irradiance necessary to

to give an excited state population density of $n_2^{\max}/2$.

For this case the ionizing laser sampling function is not very important since the time averaged value is directly proportional to the instantaneous value.

B-3. Non-Steady State Case

In the non-steady state case, the instantaneous population density of the excited state during the laser pulse can be obtained from Equation (IV-8):

$$n_2 = n_T B_{12} E_d \left[\frac{1 - \exp[-(a+bE_d)t]}{(a+bE_d)} \right] \quad (12)$$

The average population is then found by integrating Equation (IV-12) over the sampling interval of the N_2 laser (discussed in section B-1):

$$\bar{n}_2 = n_T B_{12} \left(\frac{E_d}{a+bE_d} \right) \left[1 - \left(\frac{1 - [\exp-(a+bE_d)t_0]}{(a+bE_d)t_0} \right) \right] \quad (13)$$

At low values of E_d , $a \gg bE_d$ so Equation (IV-13) reduces to

$$\bar{n}_2 = \frac{n_T B_{12} E_d}{a} \left[1 - \left(\frac{1 - [\exp(-at_0)]}{at_0} \right) \right] \quad (14)$$

If the exponential is expanded in a Maclaurin series, the result is

$$\bar{n}_2 \cong n_T B_{12} E_d \left[t_0 \left(\frac{1}{2!} - \frac{1}{3!} (at_0) + \dots \right) \right] \quad (15)$$

As in the steady state case, Equation (IV-15) implies that the ion signal should be directly proportional to laser power in the limit of low spectral irradiance if constant laser pulse length is assumed.

At higher laser powers, i.e. where $bE_d > a$, Equation (IV-13) becomes

$$\bar{n}_2 \cong n_T \frac{B_{12}}{b} \left[1 - \left(\frac{(1 - \exp[-bE_d t_0])}{bE_d t_0} \right) \right] \quad (16)$$

At very high powers, the second term in parentheses goes to zero, and the average value of n_2 reaches a limit (as in the steady state case) of

$$\bar{n}_2 = n_T \left(\frac{g_2}{g_1 + g_2} \right) . \quad (17)$$

For the non-steady state case the saturation power density, where $E_d = E_s$, is given by

$$E_s \cong \frac{1}{bt_0} . \quad (18)$$

C. Experimental

C-1. Apparatus

All power dependence measurements described were obtained with the experimental arrangement described in Chapter II. The H_2 - O_2 -Ar flame was used in all cases. The laser dyes used have been described previously (Chapter III, Table 3-1).

C-2. Reagents

Solutions were prepared as described in Chapter III.

C-3. Laser Power Attenuation

Laser power attenuation was accomplished with a set of metallic neutral density (ND) filters (Model 5023, Oriel Corp., Stamford, CT). Their nominal absorbances, as supplied by the manufacturer, are given in Table 4-1 along with the absorbances measured at the wavelengths used in the DLI studies. These were obtained through absorbance measurements performed with a commercial UV-VIS spectrophotometer (Model Cary 15, Varian Assoc., Inc., Palo Alto, CA).

C-4. Experimental Procedure

In actual experiments the lasers were first aligned so their focal points were coincident. The dye laser focusing lens was then moved to maximize the DLI signal. In the most recent studies (involving Li, Ca and Sr) it was found that defocusing the dye laser to a spot size of 0.5 cm diameter at the point of focus of the N₂ laser was most effective. For both the Na and In studies, a tightly focused dye laser beam produced the best results.

Laser power varied from day to day and alignment to alignment. In fact, small variations could be expected during the course of any experiment. Because of this, measurements were taken in bracketed sets to assure validity. That is, for each set of measurements the magnitude of the ionization signal under a standard set

TABLE 4-1. Neutral Density Filter Characteristics.

Nominal Absorbance	----- Actual Absorbance at Stated Wavelength (nm) -----									
	<u>337.1</u>	<u>404.4</u>	<u>410.0</u>	<u>422.7</u>	<u>455.5</u>	<u>460.7</u>	<u>589.0</u>	<u>670.7</u>		
0.1	0.168	0.088	0.088	0.087	0.083	0.082	0.079	0.081		
0.2	0.268	0.182	0.182	0.182	0.180	0.180	0.177	0.177		
0.3	0.357	0.288	0.289	0.291	0.293	0.294	0.302	0.307		
0.4	0.407	0.349	0.351	0.354	0.360	0.361	0.373	0.378		
0.5	0.588	0.514	0.517	0.518	0.520	0.520	0.517	0.512		
1	0.961	0.941	0.947	0.958	0.980	0.983	0.998	0.992		
2	2.15	2.06	2.06	2.06	2.06	2.06	1.96	1.90		
3	—	2.91	2.91	2.90	2.89	2.88	2.74	2.66		

of conditions was observed both before and after the measurements were taken, and, if these did not match, within experimental error, the set was not used.

In all experiments in which the dye laser power was varied, the baseline from which ionization signals were measured was taken as the signal obtained with the dye laser completely blocked (i.e. $E_d = 0$). Signals arising from broadband laser action were found to be due to resonant processes (the same as those under study), and no compensation for them was necessary. Similarly, in experiments in which the N_2 laser power was varied, the baseline was taken as the N_2 laser blocked condition (i.e. $E_i = 0$). Thus the effects of collisional processes were not included, and the true effect of the N_2 laser was observed.

Charge sheathing effects, which would make meaningful power dependence studies impossible (see Chapter V) were avoided through careful choice of analyte concentrations (see Chapter III. Section B).

D. Results and Discussion

In this section the results of experiments involving the effects of the exciting and ionizing laser powers in DLI are discussed. Since the major assumption which allows the use of a two level model involves the ionizing (N_2) laser, the effects of this laser are discussed first. The effects of dye laser power in LEI experiments (both resonant and non-resonant) and the effects of the

N_2 laser on off-resonant background ionization signals are also discussed.

D-1. Effect of Ionizing Beam Power in DLI

The discussion presented in the first two sections of this chapter indicated that the DLI system could be treated with a two level model as long as collisional and photo-ionization processes did not significantly drain the population of the excited level. The results of the last chapter show that in the cases of Li, Na, Ca and Sr, with the dye laser tuned to the major resonance lines, photo-ionization dominates collisional ionization by at least two orders of magnitude. All that remains to justify the two level assumption under our experimental conditions, then, is to show that the excited state population in the ionization region is not greatly affected by the nitrogen laser beam. To this end, a number of experiments were performed. In DLI experiments involving all of the above-mentioned analytes the dye laser power level was held at a constant level and the N_2 laser power was varied. The results of the Li study were typical and are presented in Figure 4-2. In all cases the ionization signal was found to be linearly dependent upon N_2 laser power, especially at the higher power levels. If there was a significant depopulation of the excited state caused by the N_2 laser, a negative deviation would be expected at the high power end due to optical saturation of the photoionization process. Obviously, this was not found.

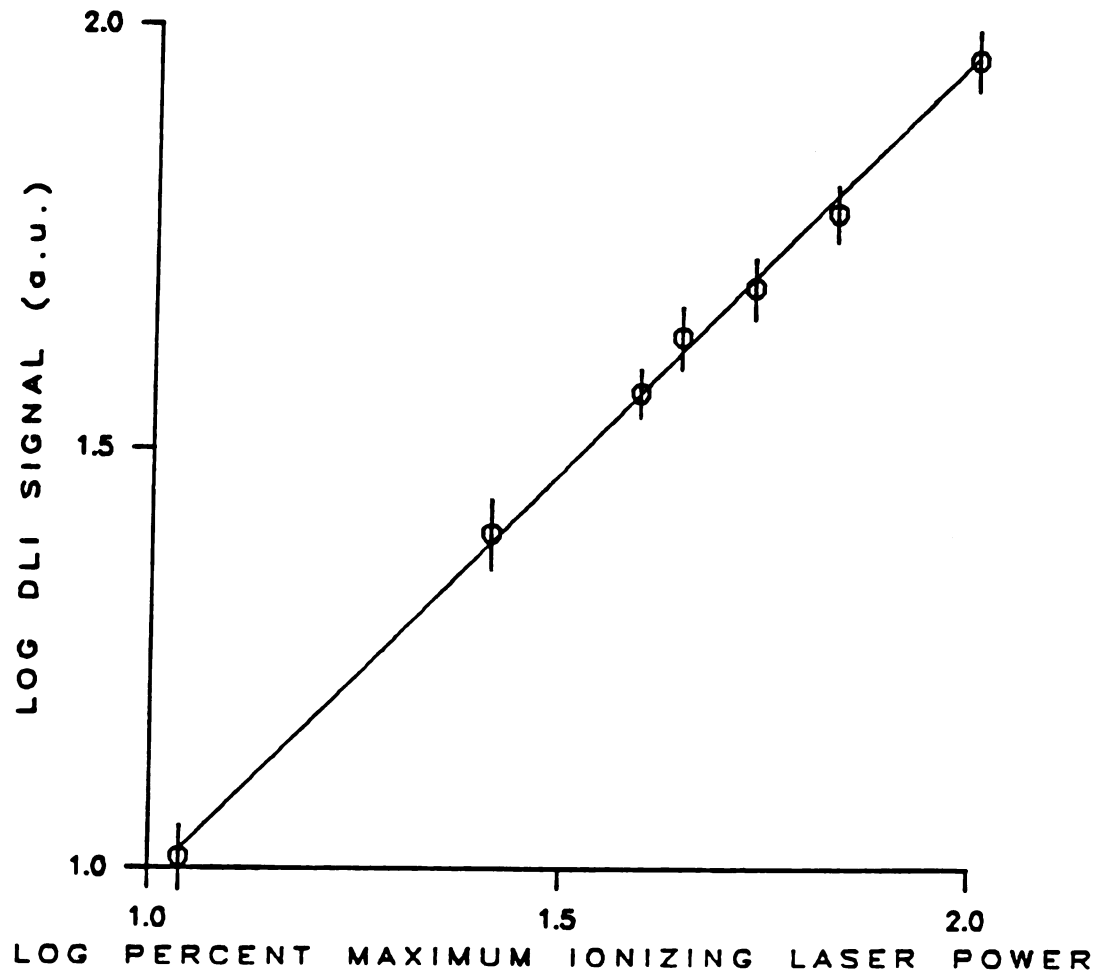


Figure 4-2. Dependence of DLI on ionizing laser power (Li as analyte).

Lin¹⁸ found a negative deviation at the high power end in one of his studies but the elevated concentration he used suggests that this was due, in fact, to charge sheathing effects.

Next, a dye laser power dependence curve was obtained with Li as the analyte and with full nitrogen laser power. The nitrogen laser power was then reduced to 54% of its original value with the 0.2 ND filter, and the dye laser power dependence curve retaken. As expected, the absolute magnitudes of the signals in the second part of the experiment dropped by about 54%. When normalized, however, these curves were found to be almost exactly coincident. The data are shown in Figure 4-3. This finding is consistent with the assumption under study. If the excited state were significantly depopulated by the N₂ laser, the dye laser power necessary for saturation would be higher at higher N₂ laser powers. There is no evidence of this type of behavior.

From the above it is surmised that the assumption justifying the use of a two level system is reasonable. This is also consistent with the calculations of Lin¹⁸. He finds for Na that the collisional ionization rate constant is on the order of 10^4 sec^{-1} . Experimental results indicate that the rate constant for photoionization must be about two orders of magnitude greater than this. For a rate constant of this size the value of the fraction of the total atomic population which is

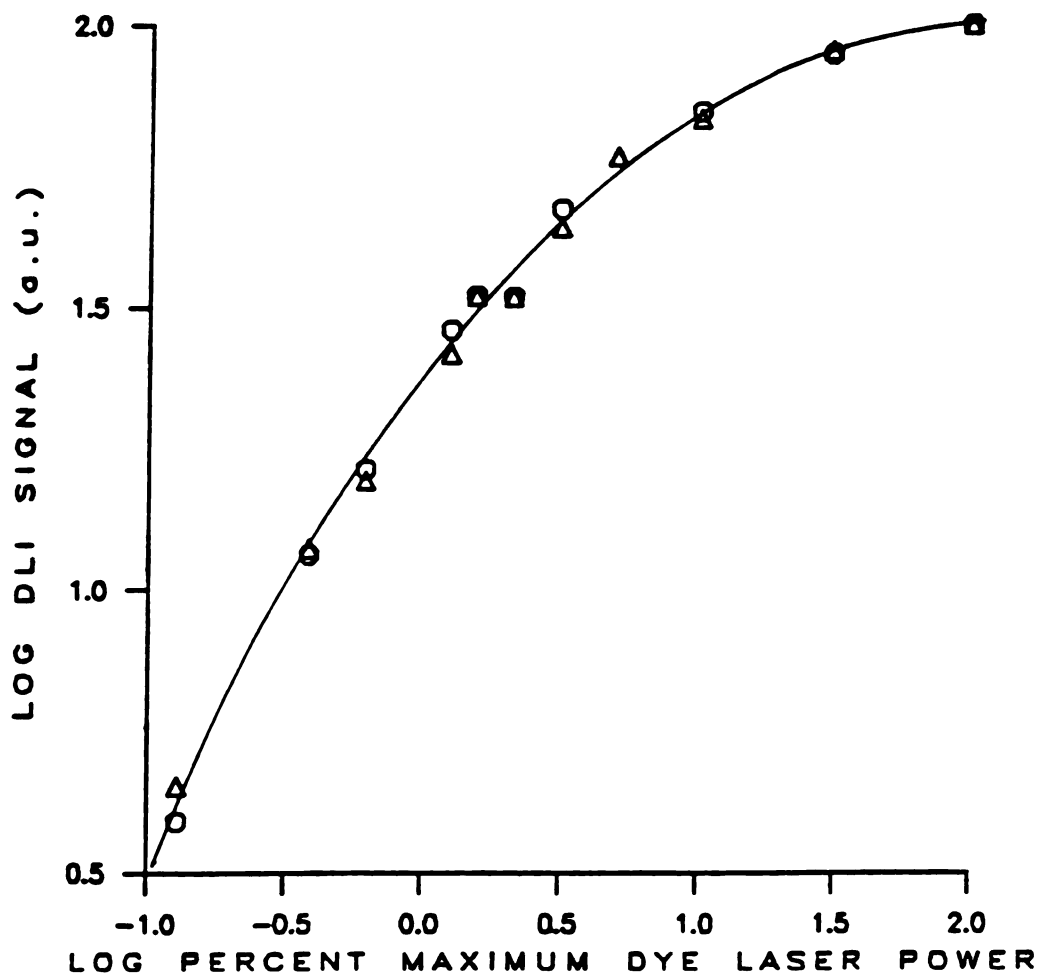


Figure 4-3. Dependence of DLI on dye laser power (Li as analyte). (○) ionizing laser at full power; (Δ) ionizing laser at half power.

ionized should be between 10^{-3} and 10^{-2} , which is negligible. It is therefore also expected that the two level model should be valid for at least another order of magnitude increase in the photoionization rate constant (due either to increased laser power or a better energetic match in the ionizing beam (i.e. smaller E_{0S} , see Chapter III)). After this the so-called "electrical saturation" must be considered. This occurs when the fraction of analyte atoms ionized approaches unity. Other authors have suggested the possibility of this type of saturation in LEI experiments in which the laser populated level lies very near the ionization continuum^{68,102,103}.

D-2. Dye Laser Power Dependence in DLI

The results of one dye laser power dependence study have already been shown in Figure 4-3. Here, the dye laser power was varied at constant N_2 laser power and with Li as the analyte. This study was repeated for a wider range of dye laser powers, and the results are presented in Figure 4-4. Results of similar studies in which Sr and Ca were used as the analytes are shown in Figures 4-5 and 4-6 respectively. These all resemble typical saturation curves found in LEAF experiments¹²³. All exhibit an initial linear region followed by a region in which the ionization signal varies nonlinearly with laser power. Finally a region in which signal magnitude is nearly independent of laser power is observed. In the Li and Sr experiments the initial region actually exhibits

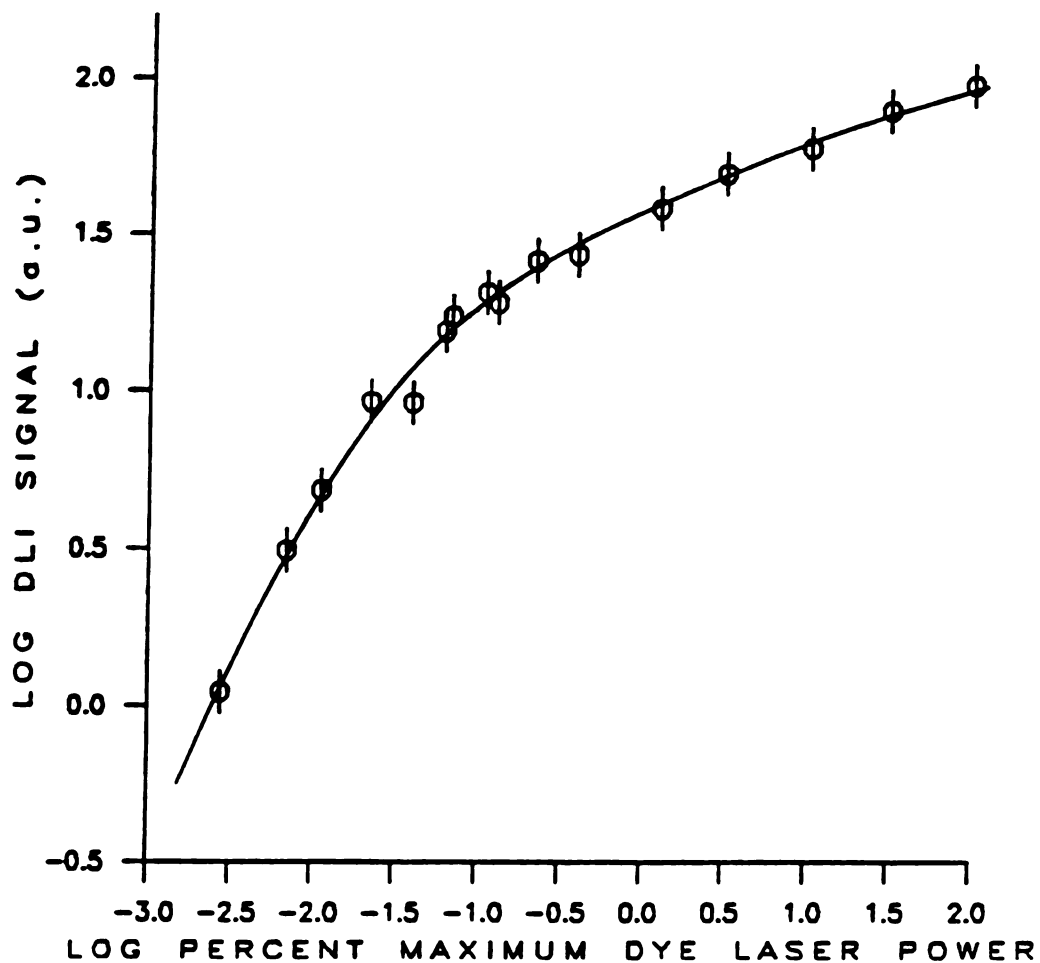


Figure 4-4. Dependence of DLI on dye laser power (Li as analyte; extended dye laser power range).

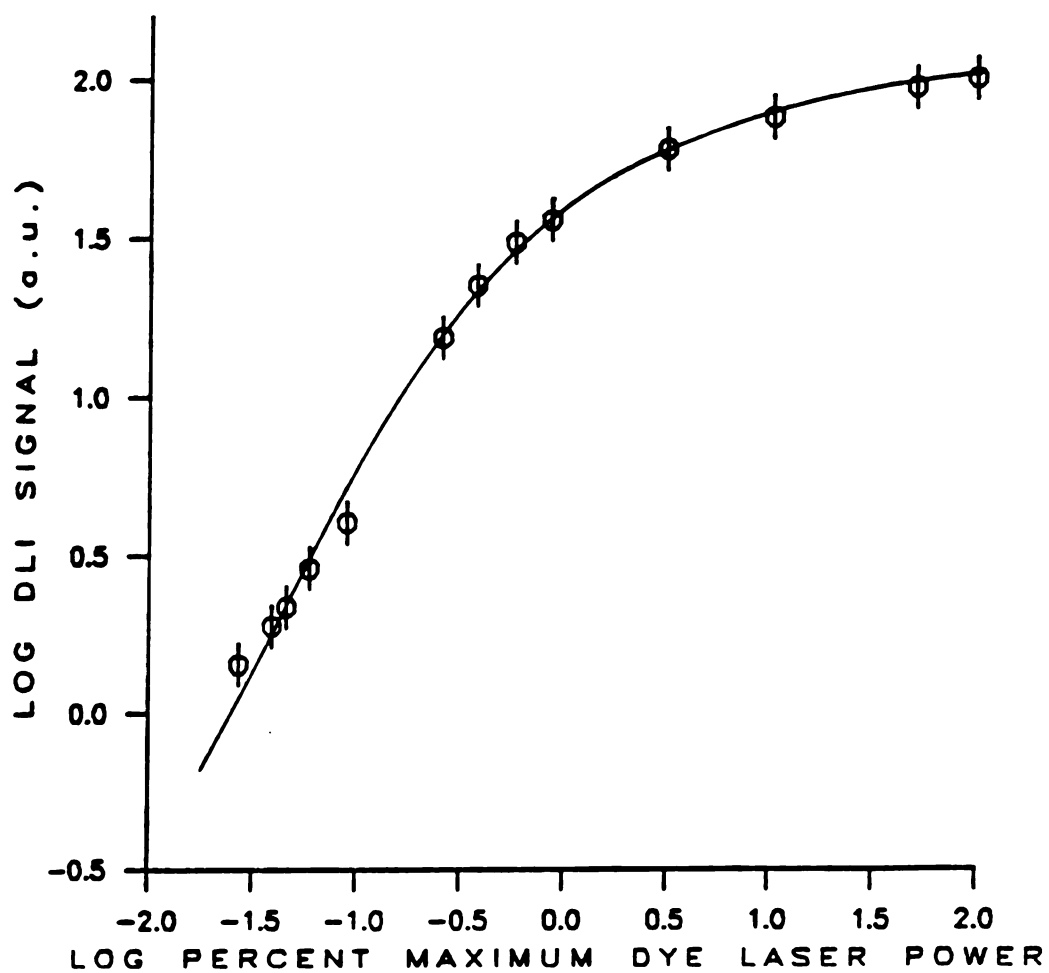


Figure 4-5. Dependence of DLI on dye laser power (Sr as analyte).

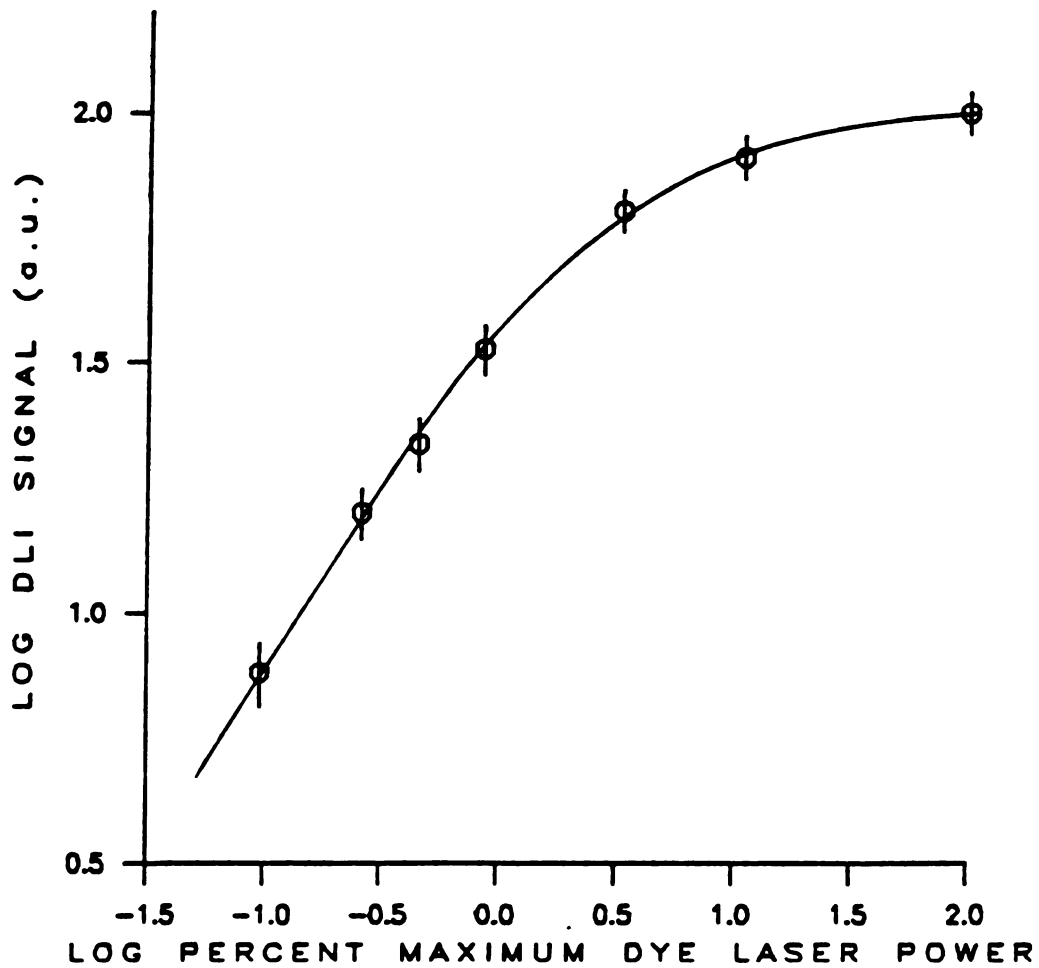


Figure 4-6. Dependence of DLI on dye laser power (Ca as analyte).

a slope of one indicating the total absence of saturation. This is exactly the behavior expected from a two level system as described in the theoretical section.

If it can be assumed that complete saturation of the excited state is achieved with the highest available laser power, an approximate value of the saturation power densities in each case can be determined. This is the power density at which the signal is one half of its value at complete saturation. These all lie in the range of 0.5 to $5 \text{ W cm}^{-2} \text{ Hz}^{-1} \times 10^9$. This is in reasonable agreement with the values calculated by DeOliveras¹²³. For Ca and Sr she calculated 1.6 and $1.2 \text{ W cm}^{-2} \text{ Hz}^{-1} \times 10^9$ in an air acetylene flame. Other studies in the same work showed that saturation power values should be lower in the $\text{H}_2\text{-O}_2\text{-Ar}$ flame than in the air acetylene flame and also under the fuel-rich conditions we normally employ. Her calculations, however, were made for a wider pulse-length laser and assumed a laser bandwidth narrower than ours. The latter should not be a major consideration due to the line broadening caused by the N_2 laser¹⁸.

Two other cases of dye laser power dependence were studied. For Na at 589.0 nm the curve was similar in shape to those found for Li, Ca and Sr but did not display as high a degree of saturation. Similar data have been reported by Lin¹⁸. DeOliveras reported similar results in LEAF experiments.

The In transition at 410.1 nm showed no signs of saturation. The highest obtainable dye laser power, however, was considerably lower than that obtained in other wavelength regions so it is presumed that only the low power end of the excitation curve is accessible in this case.

D-3. Dye Laser Power Dependence in LEI

The effect of dye laser power in LEI was studied for four single-photon resonant cases, one single-photon non-resonant case and one two-photon case in which the two photons combined to excite a single-photon forbidden transition. In LEI as in DLI the laser coupled levels should be isolated and amenable to the two level treatment previously presented unless collisional ionization becomes a significant drain on the excited state population. This is the case of "electrical" saturation which was discussed earlier (see D-1).

Before beginning a discussion of the experimental results, a point made in Chapter III will be reviewed. It was observed that the DLI signal arises from a small area of the flame around the focal point of the N_2 laser. The LEI signal, however, occurs across the flame and, since the dye laser power is not constant across the flame, it may be expected that dye laser power dependence curves will not exhibit as high a degree of saturation as seen in the DLI curves.

In the first experiment Na was used as the analyte and the dye laser power ($\lambda = 589.0$ nm) was varied. The results of the study are shown in Figure 4-7. The plot is seen to be roughly linear (the scatter at the low power end is due to the low level of signal at these laser powers). The slope, however is not unity, but about 0.8; this indicates that in this region of laser power some saturation effects are occurring.

Similar studies were performed using K, Cs and In as analytes. For each the dye laser was tuned to a major resonant transition (i.e. K(4s $\rightarrow$ 4p; 404.4 nm), Cs(6s $\rightarrow$ 7p; 455.5 nm) and In(5p $\rightarrow$ 6s; 410.1 nm)). The results obtained in the K experiment were typical and are shown in Figure 4-8. In each case the log-log plot of the data was linear with a slope of almost one. This indicates no optical or ionization saturation was occurring. The results of these studies might have been predicted from the data given in Table 3-2. Both the Einstein A and B coefficients are oscillator-strength dependent as

$$A_{21} = \frac{8\pi^2 e^2}{mc\lambda_0^2} \left(\frac{g_1}{g_2} \right) f$$

and

$$B_{21} = \frac{\lambda_0^3}{8\pi h} A_{21}$$

In the above, f represents the oscillator strength of the transition and the other terms take on their usual meanings. As noted previously, the saturation power

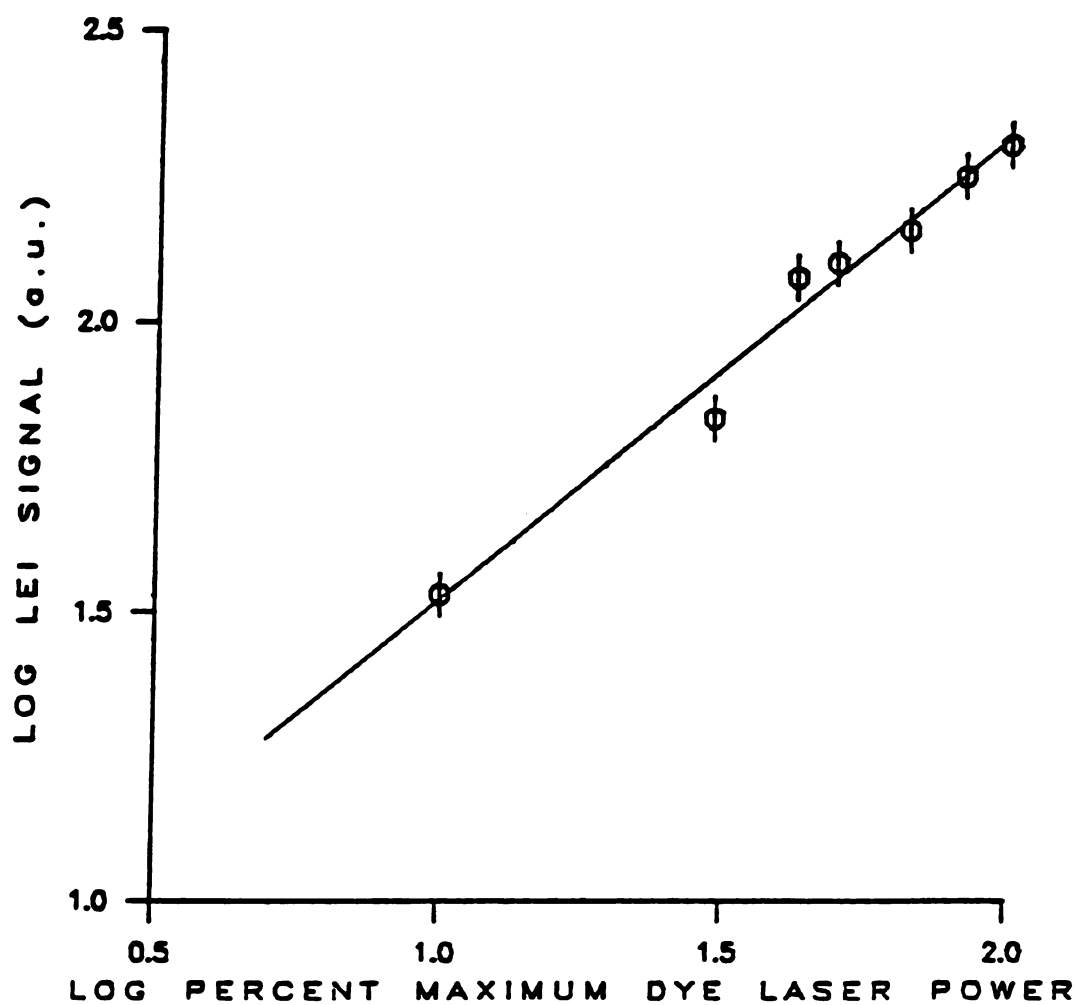


Figure 4-7. Dependence of LEI on dye laser power (Na as analyte).

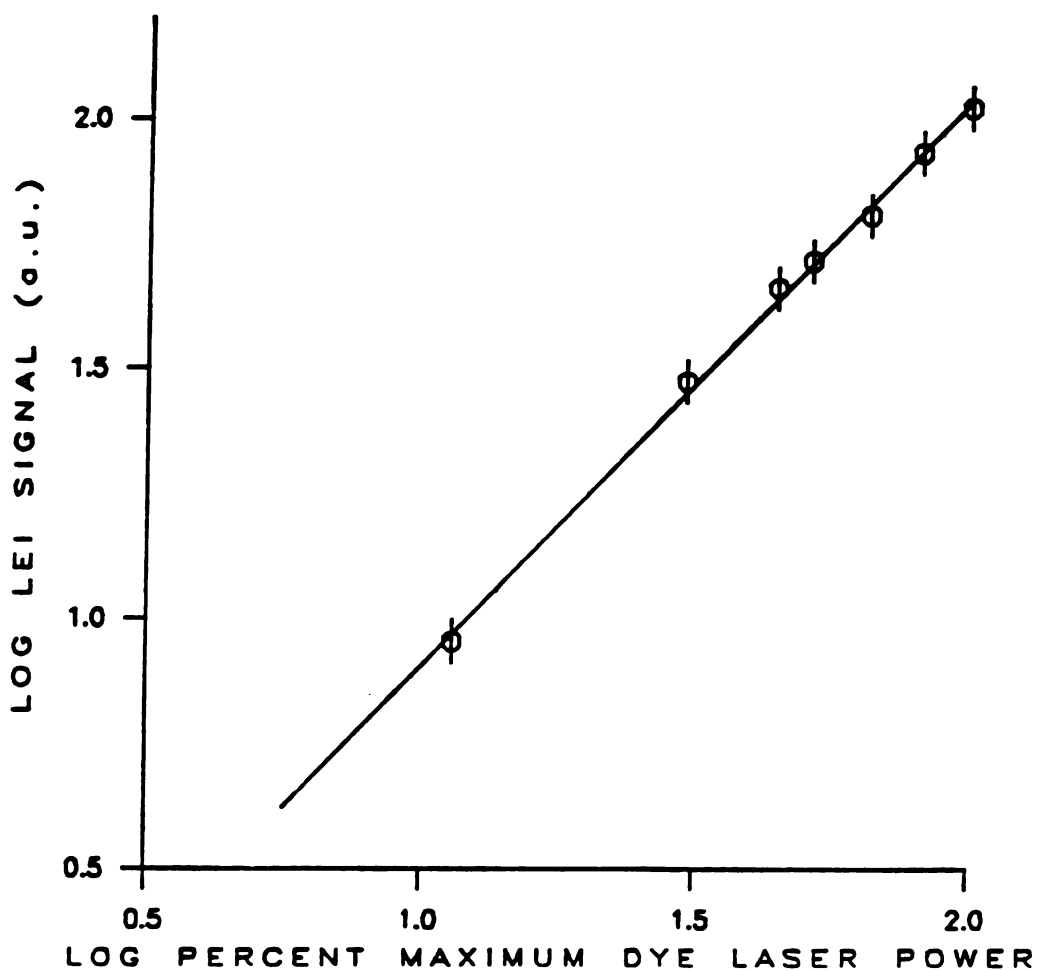


Figure 4-8. Dependence of LEI on dye laser power (K as analyte).

density in the case in which steady is reached is given by

$$E_s = a/b = \frac{A_{21} + k_{21}}{[1 + (g_1/g_2)B_{12}]}$$

This is more commonly expressed as

$$E_s = \frac{A_{21}}{gYB_{12}}$$

in which g has replaced $(1+g_1/g_2)$ for simplicity and Y is the fluorescence efficiency factor given by

$$Y = \frac{A_{21}}{A_{21} + k_{21}}$$

From the above it can be seen that the saturation power density becomes independent of oscillator strength, in the steady state case, only when the fluorescence efficiency factor approaches unity (i.e. when collisional deactivation becomes unimportant). This is not a common occurrence.

In the non-steady state case the saturation power density is approximated by

$$E_s \cong \frac{1}{bt_0}$$

and so is always dependent on oscillator strength. For each of the abovementioned analytes the oscillator strength for the laser-excited transitions is considerably lower than those seen in the cases in which saturation was observed.

The non-resonant transition of Ca($3d \rightarrow 7p$; 424.0 nm) gave the smallest energy defect studied so ionization saturation would be most likely here. The log-log plot was found to be linear, however, ruling this out. The slope of the line was found to be higher than those observed previously (i.e. ~ 1.5) and this indicates that multiphoton processes may be occurring.

Finally the two photon transition in Na at 578.7 nm ($3s \rightarrow 4d$) was studied. Here, the log-log plot was found to be linear and had a slope of two as expected. The low cross-section expected for two photon absorption makes saturation improbable and none was in evidence in the study.

D-4. Off-Resonant Photoionization

Background ionization signals caused solely by the nitrogen laser were first observed in studies of electrical interferences (see Chapter V). Both K and Cs are common matrix components in real samples and both were found to produce background signals when high concentrations were nebulized into the flame. Nitrogen laser power dependence studies were performed on both. The results of the Cs experiment are presented in Figure 4-9. Here the plot is seen to be linear and the slope is nearly two (~ 1.8). Similar results were obtained with K as the analyte. These results indicate that the signal arises from off-resonant two photon photoionization of the species. No saturation

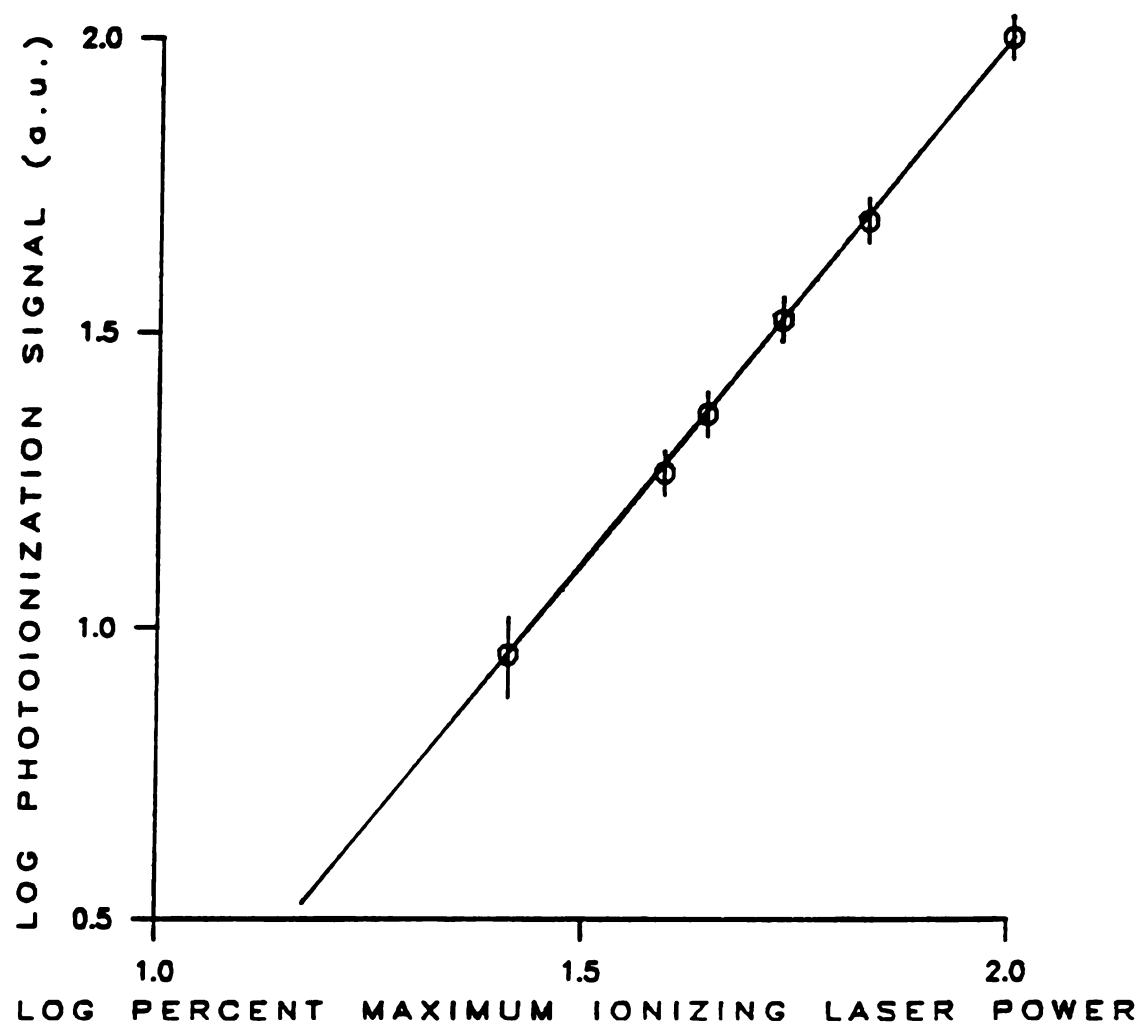


Figure 4-9. Off-resonant photoionization of Cs.

effects are expected (due to the low cross-sections two photon transitions normally have), and none were observed.

CHAPTER V

DUAL LASER IONIZATION IN FLAMES: A SEARCH FOR IONIZATION INTERFERENCES

A. Introduction

Almost since its inception, LEI has been known to suffer from electrical interferences caused by easily ionized matrix components^{13,69,70}. The nature of this interference has been explored in detail by Turk⁷¹. His findings indicate that thermal ionization of the matrix causes an increase in the positive space charge near the cathode. The applied potential falls rapidly across this charge sheath¹²⁵, which decreases the collection efficiency. Turk also tested a water cooled cathode that could be immersed in the flame⁷¹. He found that keeping the laser irradiated region near the cathode (i.e. within the cathode fall) was effective in reducing matrix interferences as in this region the ions "see" the electric field. More recently, pulsed signal collection has been tried and found ineffective in reducing matrix interferences⁷⁴; it was suggested that time resolution may be effective, as in some cases analyte and matrix component concentration development rates differ.

Also, LEI with cw laser excitation has been found to suffer much less from electrical interferences because of the radically different nature of the charge collection process⁷³.

As DLI is closely related to LEI (with pulsed laser sources) it was of interest to study the effects of common matrix components on the DLI signal and to compare these results with those obtained from LEI experiments. This chapter presents the results of those studies.

B. Experimental

B-1. Apparatus

The experimental system used in these studies has been described completely in Chapter II.

B-2. Reagents

All solutions were prepared from reagent grade chemicals. When possible these were dissolved directly in distilled, deionized water. The chloride salts of Na, Li, and K were used as was the bromide salt of Cs and the nitrate salt of Sr. Solutions for studies involving Zn and Mg were prepared both with the hydrated sulfates of these metals and by dissolution of the pure metals in HCl followed by neutralization with NH_4OH . For studies of anionic interferences, ammonium salts of various anions were used. All solutions, unless otherwise noted, contained an analyte concentration of 10 ppm.

The following laser dyes were obtained commercially and used without further purification: Rhodamine 6G

(Eastman Kodak Co.; 7.5×10^{-3} M in ethanol) for Na analysis; Coumarin 460 (Exciton Chemical Co., Inc.; 1×10^{-2} M in ethanol) for Sr analysis; and DCM (Exciton Chemical Co., Inc., 5×10^{-3} M in DMSO) for Li analysis.

B-3. Data Treatment

In most cases data were collected with the boxcar integrator in the exponential averaging mode and the dye laser tuned to the resonance line of the analyte of interest (i.e., 589.0 nm for Na, 670.8 nm for Li and 460.7 nm for Sr). The interference studies are reported as percent signal recovery versus concentration of the potential interferent. Percent signal recovery is defined in Equation (V-1) as

$$\% \text{ Recovery} = (S'_A / S_A) \times 100 \quad (1)$$

where S'_A is the analytical signal in the presence of the potential interference, and S_A is the analytical signal obtained from a solution containing no added interferent. Because of the presence of background ionization of some interferents, in most cases due to off-resonant N_2 -laser-induced multiphoton ionization, background subtraction was necessary to obtain S'_A and S_A . Two methods were found to give similar results. In the first method, the dye laser was scanned across the resonance line of the analyte, and the analytical signal was obtained as the height of the resulting peak relative to the baseline away from resonance. When the matrix constituents are unknown, as in a practical

analysis, this method of background subtraction is necessary. In the second method the analytical signal S_A' in the presence of the interferent, was obtained as the total signal S_T' in the presence of the interferent minus the signal S_B' from the interferent alone

$$S_A' = S_T' - S_B' . \quad (2)$$

Likewise, the analytical signal in the absence of interferent, S_A , was obtained as the total signal S_T minus that of a distilled, deionized water blank, S_B

$$S_A = S_T - S_B . \quad (3)$$

Beecause this latter method required no change in dye laser wavelength for a given analyte, it was considerably more rapid than the former method and was used in all the studies reported here.

C. Results and Discussion

Experiments were performed to demonstrate the effects of common matrix constituents on the DLI signals of various elements. The study concentrates on a search for electrical interferences. Also reported are two chemical interferences that appear to be different from those encountered in routine flame emission studies. Non-specific (physical) interferences are not discussed as they should be identical to those found in conventional spectroscopic techniques.

Electrical interferences in DLI experiments can be broken down into two categories. One type is those interferences caused by the ionization of matrix components via thermal processes in the flame. These have been described for LEI by Turk⁷¹ and this description was based, in turn, on the extensive studies of electrical phenomena in combustion systems by Lawton and Weinburg¹²⁵. Briefly, the extraction rate of electrons by the anode is much greater than that of cations due to the greater mobility of electrons in the flame. This leads to excess positive charge in the flame which builds up as a sheath around the cathode and essentially negates, or drops, the potential difference between the probes. Turk found that signal recovery could be expected only when the laser irradiated region (ionization region) was within this sheath. Results from this study indicate similar phenomena as signal recovery is highly dependent on cathode/laser beam positioning. The DLI experiment also suffers from laser-related (spectro-electrical) interference, due mainly to off-resonant multiphoton ionization of easily ionized matrix components. Oscilloscope tracings showed these signals to be combined with the signal from the analyte in a single ionization pulse. They can be compensated for, in part, by various methods (cf. section B of this chapter), but do add noise to the signal because the off-resonant multiphoton processes have extremely low cross sections (i.e. non-saturated

phenomenon) and consequently are strongly affected by pulse-to-pulse variations in laser power. The low cross sections, however, do make minimization of these effects possible, without significant signal loss, through slight defocusing of the laser beams, especially if there is saturation of the analyte transition.

Cesium was chosen as the interferent in initial studies because of its low ionization potential (3.9 eV). Cesium has no atomic transitions in the region of the analytical lines for Na or Li, but the 460.7 nm transition of Sr is quite close to the 455.5 nm transition of Cs from which large LEI signals have been obtained (see Chapters III and IV).

In Figure 5-1 the DLI and LEI percent recoveries are shown for solutions containing 10 ppm Na and varying amounts of Cs. In the DLI plot, the decrease in signal recovery with increasing Cs concentration is very gradual and does not exceed 10% even at the maximum interferent to analyte ratio of 100:1. Higher Cs concentrations were not used because flame emission studies showed that they decreased atomization efficiency significantly indicating, in all likelihood, a physical type of interference.

Although our system is by no means optimal for the performance of LEI experiments (as we use a nanosecond pulsed dye laser rather than the typical flashlamp pumped, microsecond pulsed tunable dye laser), by blocking the path of the N₂ laser to the flame, LEI experiments can

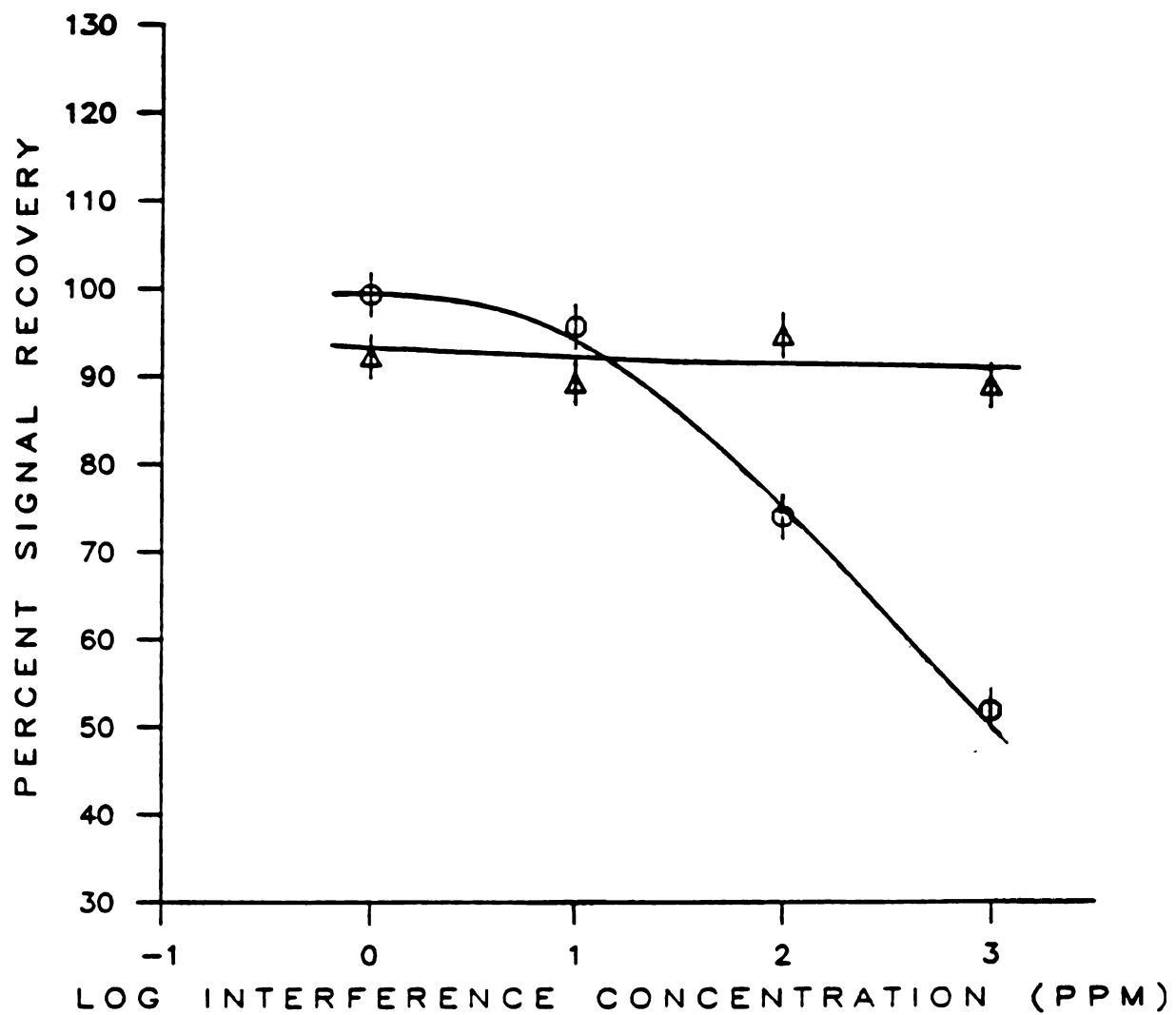


Figure 5-1. Percent signal recovery for Na versus Cs concentration, DLI (Δ) and LEI ($\bigcirc$) cases. [Na concentration: 10 ppm (Δ); 100 ppm ($\bigcirc$)].

be performed. Because the LEI signal was approximately two orders of magnitude lower than the signal obtained with DLI¹⁵, the Na concentration was increased to 100 ppm and the flame was made less reducing in order to obtain a workable signal level. The results of this study are also noted in Figure 5-1. Here signal reduction is much more pronounced and similar in appearance to those seen in early LEI experiments^{13,69,70}. It should also be understood that the maximum interferent to analyte ratio used in this study was only 10:1.

In a complementary study a high-lying transition ($3s \rightarrow 4d$) in Na was reached via two photon excitation (two photons of wavelength 678.7 nm). It has previously been observed that ionization from this level is almost completely collisional because the addition of the N₂ laser beam to the excitation region results in no significant signal enhancement¹⁵. Signal recovery on the ninety percent level was observed from the solution with the highest interferent-to-analyte ratio used in the single photon LEI experiment. Two factors contribute to this result. First, the smaller energy defect in the two photon experiment (0.84 eV as opposed to 3.02 eV) leads to decreased collisional dependence. The higher collisional efficiency should lessen the effect of ionization interferences. Also, cross-sections for two photon transitions are very low compared to those for single photon resonances, and previous results have shown that the

LEI signal from the $\text{Na}(3s \rightarrow 3p)$ transition is not fully saturated with respect to dye laser power (see Chapter IV). Thus it is reasonable to assume that in the two photon case the majority of the signal arises from a small region about the focal point where the photon flux is maximized whereas in the single photon case the signal arises from a larger region. Thus in the two photon case the collection probe could be placed near the region from which most of the ionization signal arises where collection efficiency should not be much affected by charge sheathing effects.

Figure 5-2 shows the results of DLI studies with Sr and Li as analytes and Cs as interferent. The Li data show little signal loss with increasing Cs concentration and, in fact, that there is some signal enhancement at the extremes. (It should be noted here that in all the studies performed, exact percent signal recovery varied from day to day with probe configuration, nebulizer characteristics, etc. The results reported here are typical). The Sr curve shows no significant interference out to an interferent-to-analyte ratio of 10:1. After this, however, significant signal decrease is seen. Closer examination of the background ionization signals found with the dye laser tuned to the Sr resonance at 460.7 nm gave a possible explanation for this behavior. Multiphoton ionization of Cs via two N_2 laser photons, two dye laser photons and via a combination of the two lasers was found

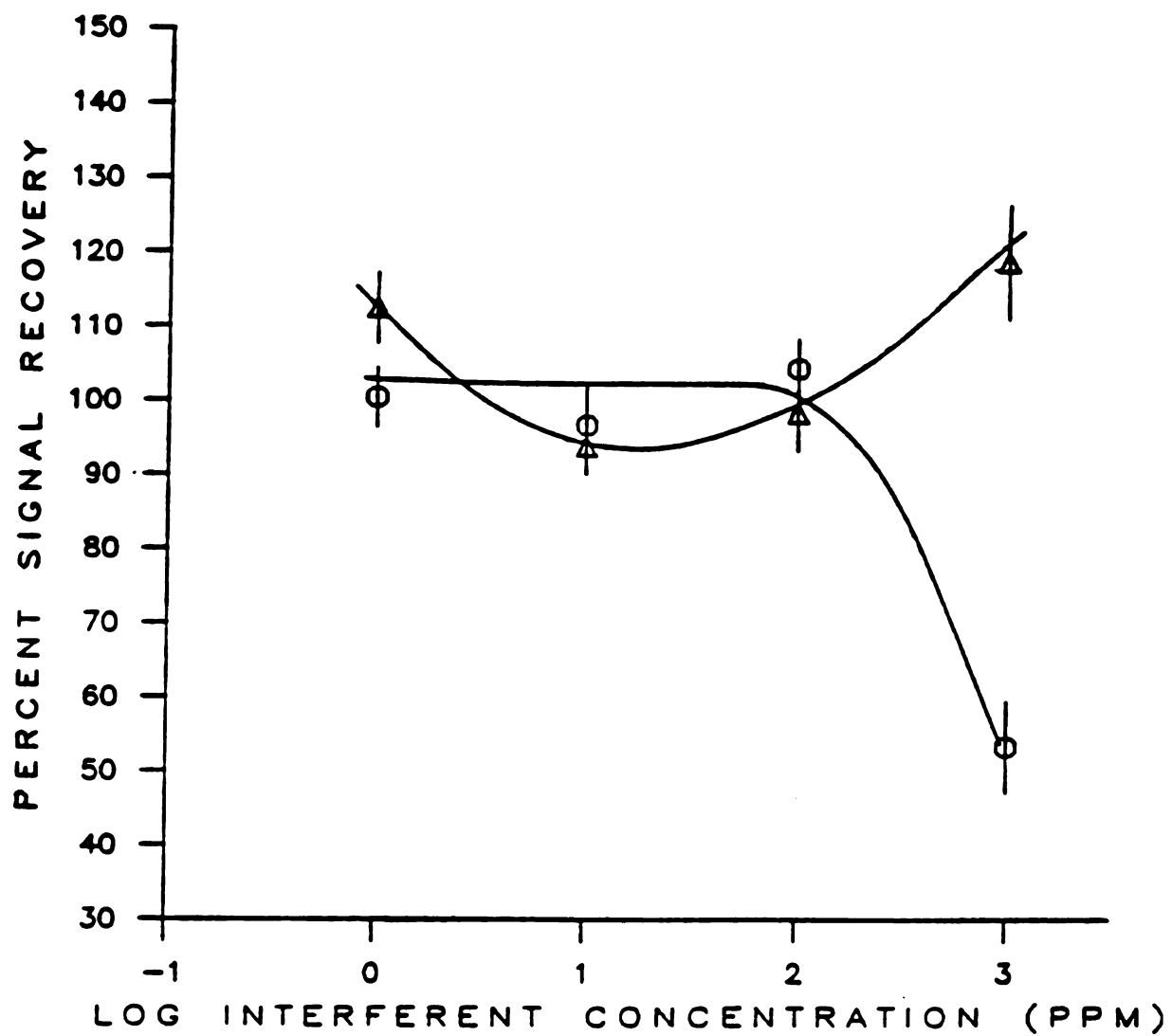


Figure 5-2. Percent signal recovery for Li (Δ) and Sr ($\bigcirc$) versus Cs concentration, DLI case.

to be occurring to a significant extent. At all other dye laser wavelengths studied, dye laser related Cs ionization was negligible compared to the photoionization produced by the N_2 laser. In this instance Cs can be looked upon as truly a "worst case" interferent.

To study the analytical utility of the DLI technique further, an analytical curve was constructed for Na in the presence of 1000 ppm Cs. This curve is shown in Figure 5-3 and is quite similar to the one obtained previously in the absence of an interferent¹⁵. As before the lowest Na concentration detected was 100 ppb (note here the interferent-to-analyte ratio of 10,000:1). The curve is linear for more than two and one-half orders of magnitude; a slight negative deviation is apparent at high concentrations. This deviation, however, is not as drastic and appears at higher Na concentrations than noted previously¹⁵. The data shown here seem to rule out recombination as an explanation for the deviation from linearity; the increased free electron concentration produced by Cs would be expected to enhance the effects of recombination and make the negative deviation more pronounced than that observed earlier¹⁵. The data are, however, consistent with charge sheathing. At high Cs concentrations, Cs should be the major contributor to the charge sheath until extremely high Na concentrations are reached. The presence of Cs should prevent Na from influencing the charge sheath (at

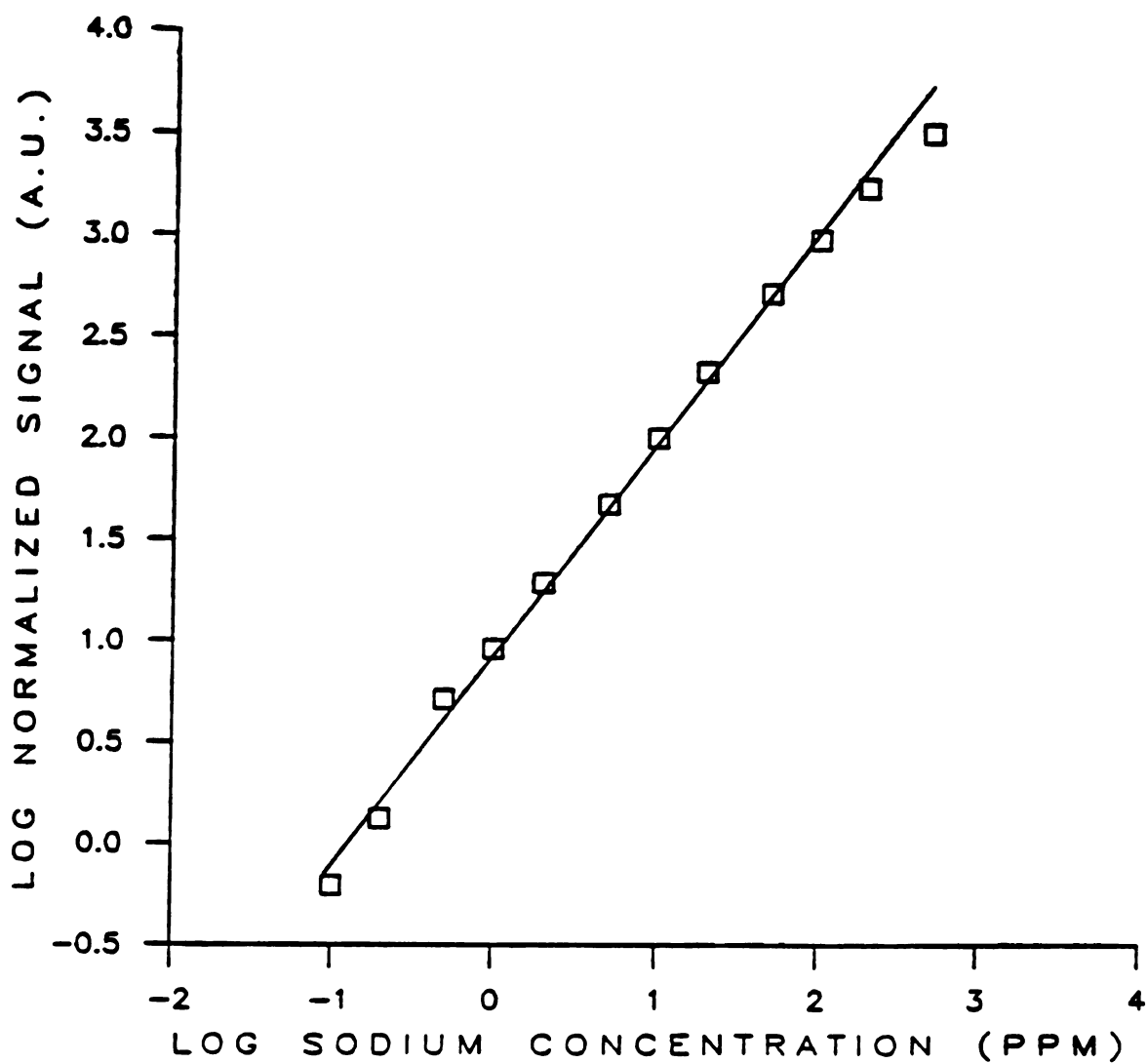


Figure 5-3. Analytical curve for Na in the presence of 1000 $\mu\text{g/g}$ Cs.

reasonable Na concentrations) and extend the range of linearity.

LEI experiments have shown that electrical interferences decrease with increasing ionization potential of the interfering species⁶⁹. Thus, the effects of cations with ionization potentials greater than that of Cs were studied. Figure 5-4 illustrates the effects of K and Li as interferents in Na analysis. Here it can be seen that K has no significant effect on the ionization signal. Lithium produces a slight signal enhancement and this varies quite gradually across the range of interference concentrations. A similar study performed with Zn and Mg is shown in Figure 5-5. The curves are nearly coincident and decline gradually at the high concentration end. Complementary flame emission studies showed that the sodium emission signal also decreases in a similar manner; this small signal reduction is thus physical or chemical, not electrical, in nature.

The data in Figure 5-5 were obtained from the metals dissolved in HCl as described in section B of this chapter. Results were also obtained with Mg and Zn solutions prepared from the hydrated sulfates, and percent signal recovery studies for these solutions are shown in Figure 5-6. The Na DLI signal from the Zn containing solutions falls off more rapidly than before, and that from Mg-containing solutions actually shows a trough with a minimum percent recovery at a Mg concentration of

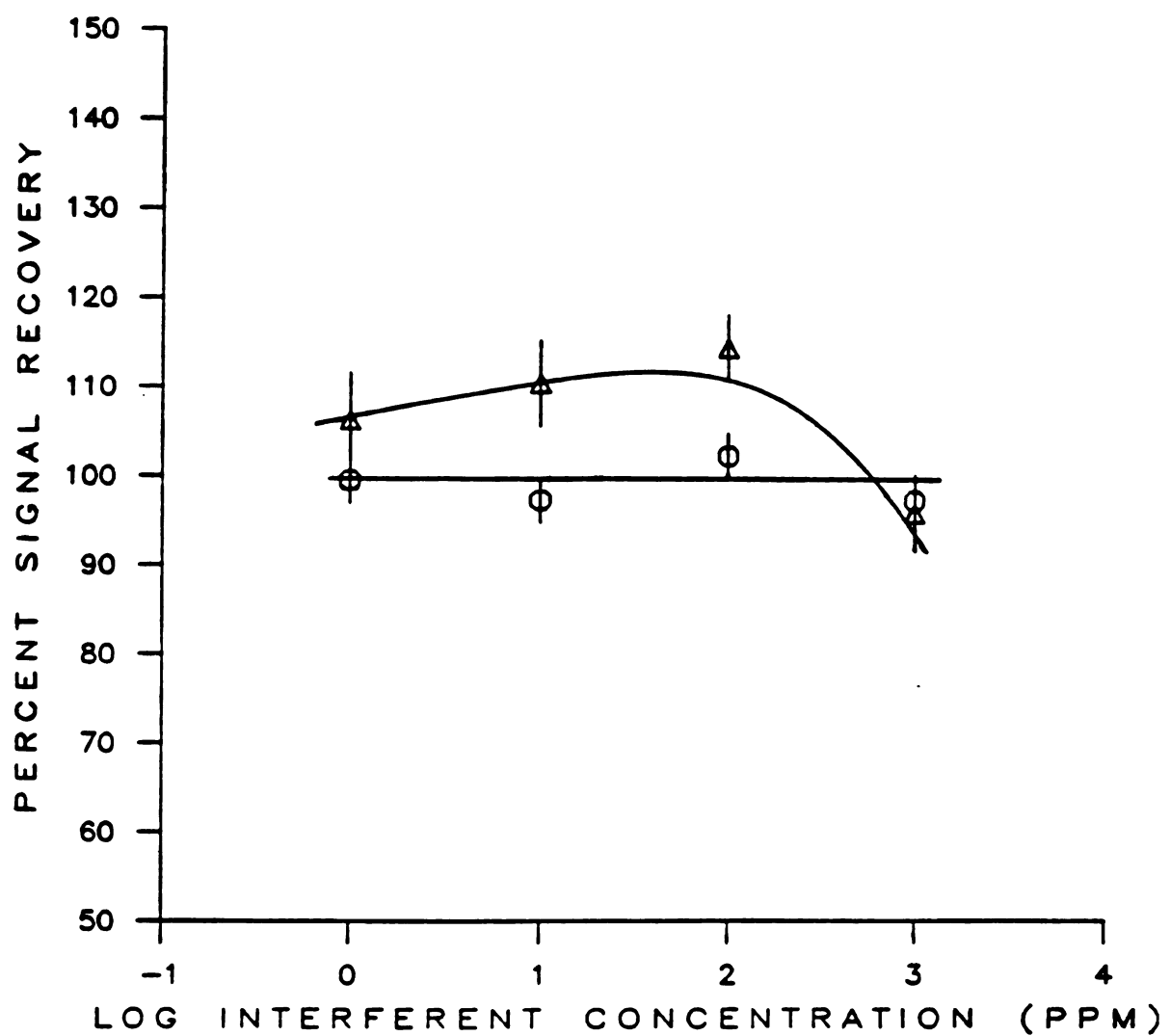


Figure 5-4. Percent signal recovery for Na versus K ($\bigcirc$) and Li (Δ) concentration, DLI case.

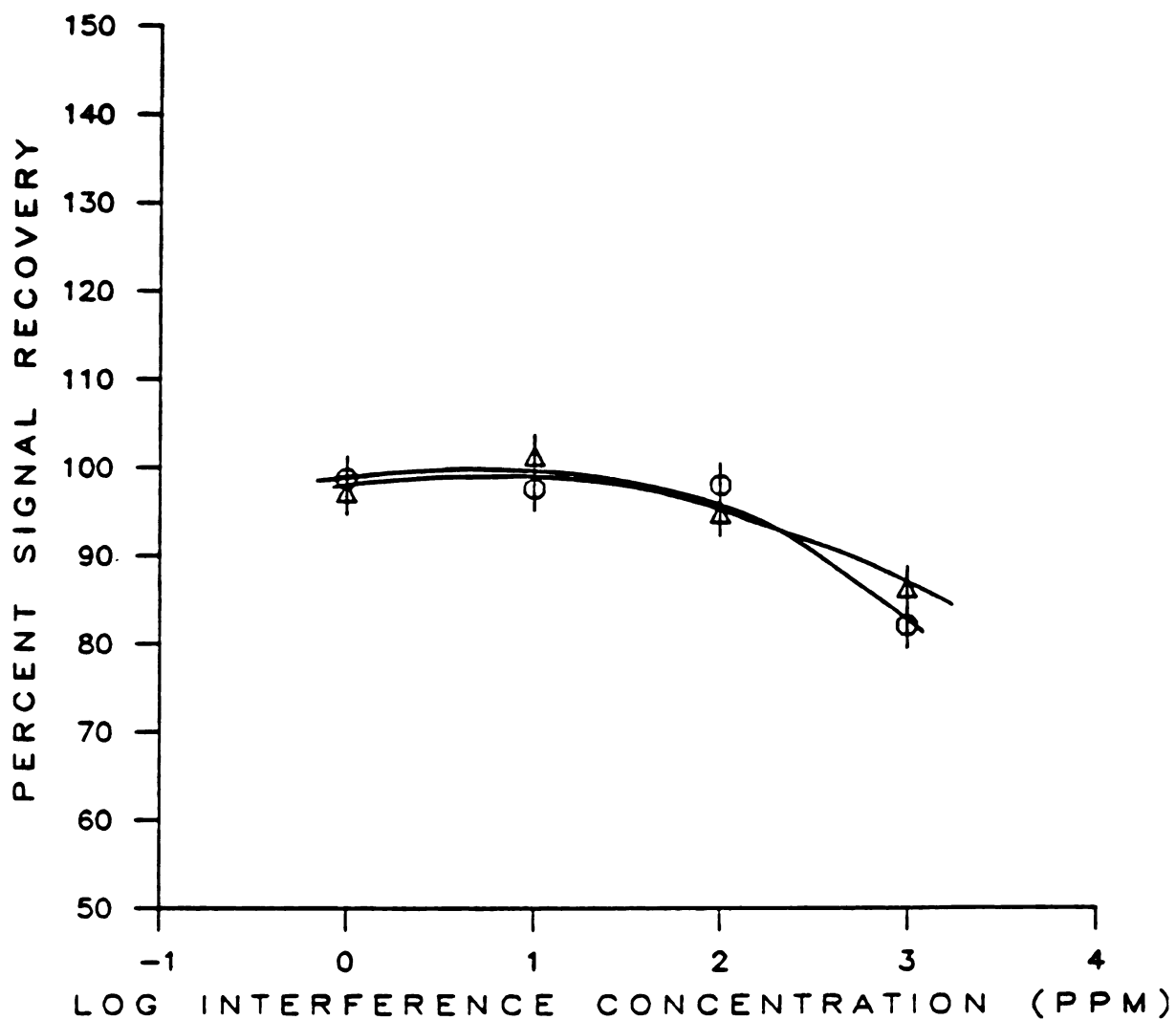


Figure 5-5. Percent signal recovery for Na versus Mg (Δ) and Zn (○) concentration, DLI case, metals dissolved in HCl followed by neutralization.

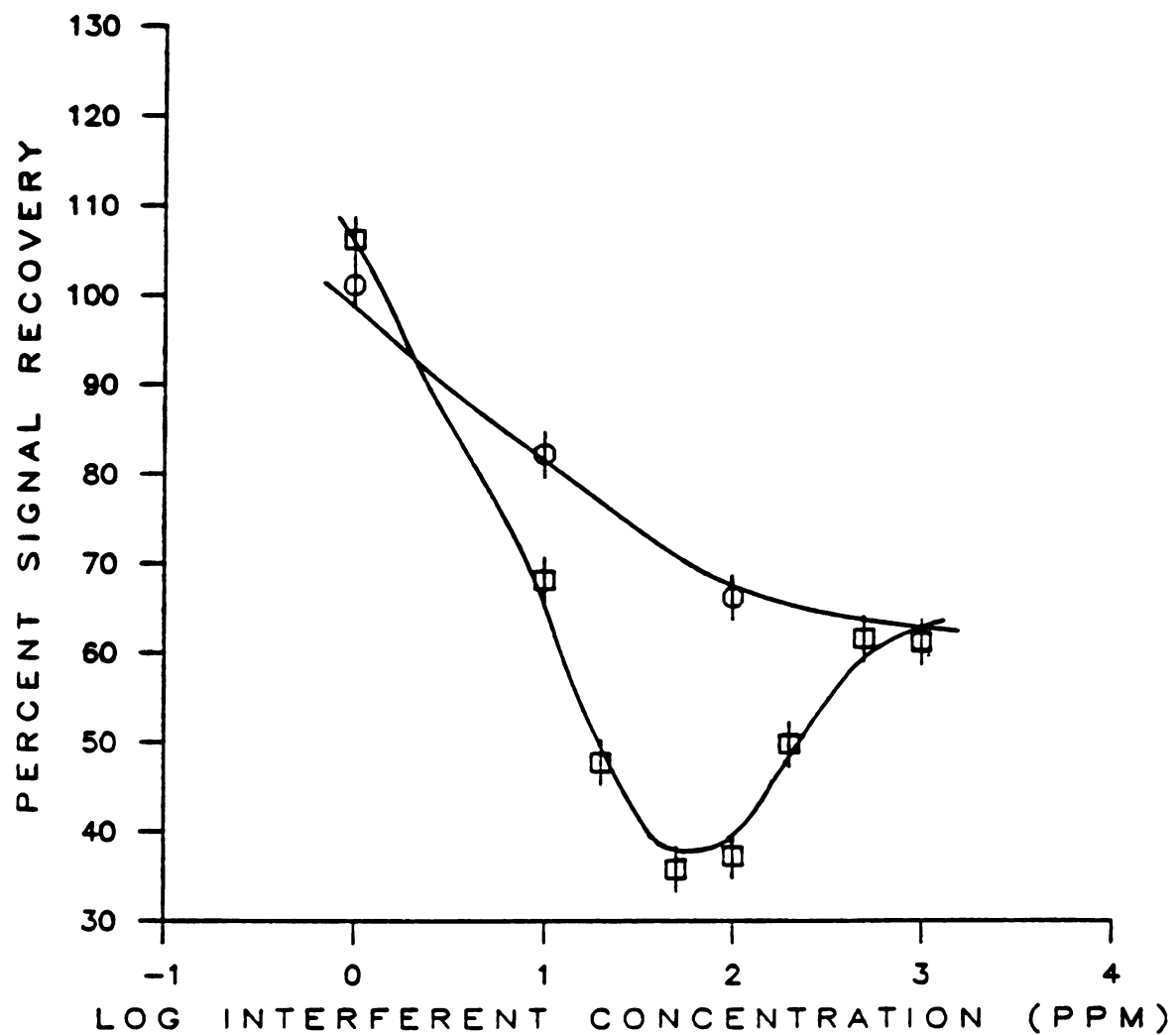


Figure 5-6. Percent signal recovery for Na versus Mg (□) and Zn (○) concentration, DLI case, metals from hydrated sulfate salts.

approximately 50 ppm. Studies of Na flame emission in the presence of Mg showed no similar effect. However, flame emission is not directly comparable to DLI because a much larger area of the flame is viewed in the emission experiment. In order to test if the results shown in Figure 5-6 could be explained by a sulfate ion effect, the Na DLI was measured in the presence of varying concentrations of $(\text{NH}_4)_2\text{SO}_4$, and the results are shown in Figure 5-7. The gradual decrease in the Na DLI signal and a similar decrease in the Na flame emission in the presence of ZnSO_4 lead us to conclude that the interference of ZnSO_4 is due to a small sulfate chemical interference, a slight decrease in nebulizer efficiency or a combination of the two. The interference of MgSO_4 is, however, intriguing, because conventional flame spectroscopic interferences usually display either an enhancing or a depressing effect, but not both. Exceptions, however, can be found in the literature. For example, Firman, in 1965, found that Fe interfered in the determination of Mg in a similar manner¹²⁶. It was suggested that this behavior was due to the formation of a series of Fe-Mg compounds of varying volatilities. In many conventional flame spectroscopic experiments, interferences of this type have been eliminated or reduced through the use of releasing agents that function by replacing the analyte atom in the non-volatile compound. For example, excess Sr, La, Nd, Sm and Yb remove the depressive effects of sulfate,

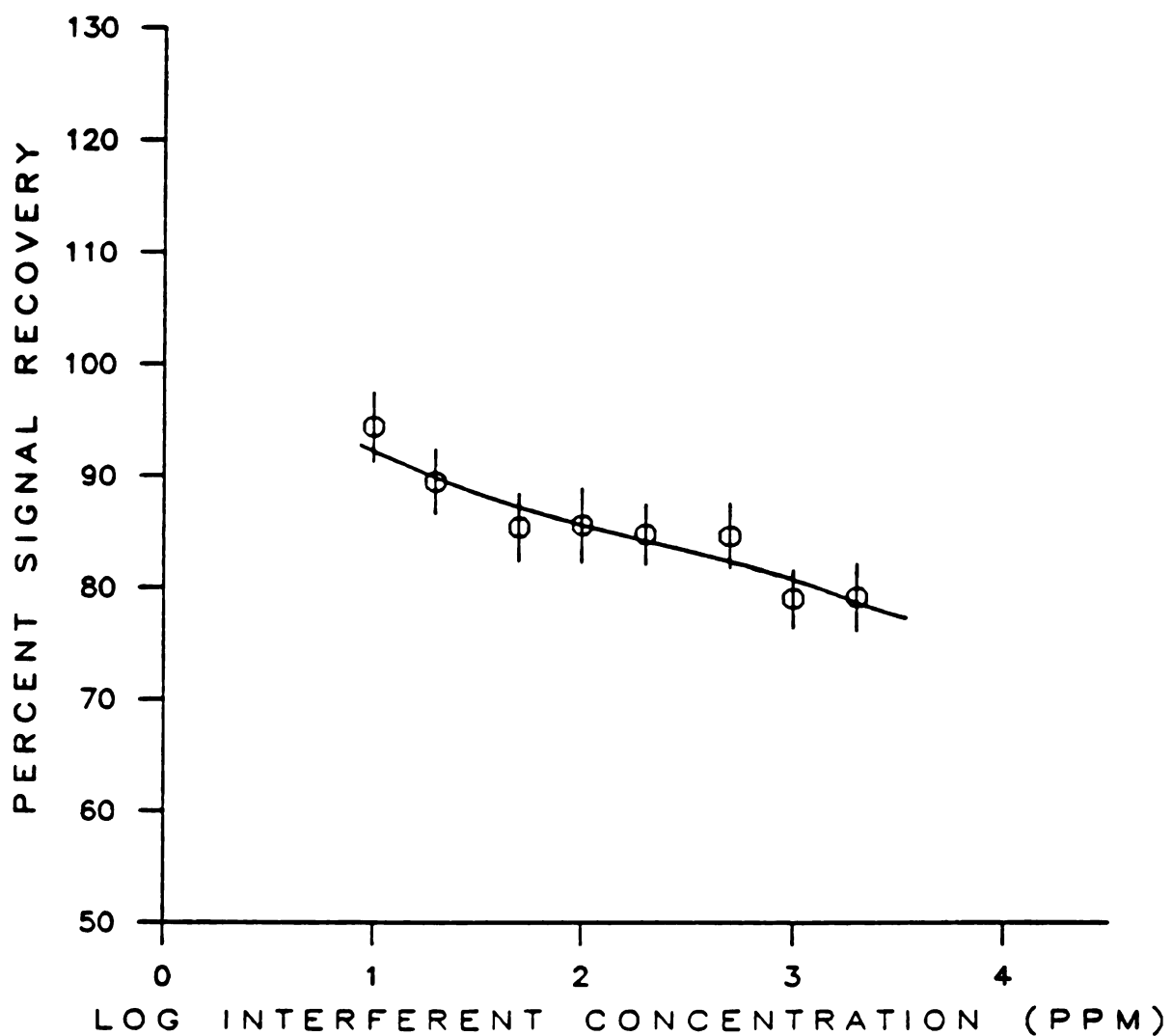


Figure 5-7. Percent signal recovery for Na versus sulfate ion concentration (from ammonium salt), DLI salt.

phosphate and aluminate ions in Ca emission¹²⁷. We tested this hypothesis by obtaining Na DLI signals from solutions of Na and Mg concentrations corresponding to the minimum in Figure 5-6, but varying in K concentration. The percent signal recovery improved with increasing K concentration from less than 40% to a maximum of approximately 70%. We thus conclude that the interference of MgSO_4 is due to the formation of non-volatile species containing Na and not to any ionization interference, per se.

D. Conclusions

In the present study the DLI technique has been extended to analytes in samples containing easily ionized matrix components. Reasonable signal recovery can be expected under normal conditions as long as the point of ionization is near the cathode. High concentrations of easily ionizable matrix components appear to extend the linearity of analytical curves, but can lead to higher noise levels because of photoionization of the matrix components.

CHAPTER VI

ANALYTICAL APPLICATIONS

A. Introduction

The ultimate goal of anyone developing a new analytical technique is to demonstrate a successful application by analysis of real samples. In early DLI experiments an analytical curve was obtained for Na in distilled, deionized water using the $\text{H}_2\text{-O}_2\text{-Ar}$ flame¹⁵. This showed that the DLI signal was linear with concentration over several orders of magnitude. The $\text{H}_2\text{-O}_2\text{-Ar}$ flame did not permit detection of signal from solutions with Na concentrations much below 100 $\mu\text{g/L}$. Further studies with Li and Ca as analytes in the same flame produced similar results. In addition, a linear calibration curve was obtained for Na in a matrix that also contained a large concentration of an easily ionized background interferent¹⁶. Attempts to determine Ca in both an unsoftened well water sample and in a blood serum sample, however, were unsuccessful when the $\text{H}_2\text{-O}_2\text{-Ar}$ flame was used. Because of this, an air-acetylene flame was incorporated into the DLI instrumental arrangement and the experiments were repeated. The air-acetylene flame

(2400-2650 K) is much hotter than the $\text{H}_2\text{-O}_2\text{-Ar}$ flame (1800-2100 K) and so provided better analyte atomization. Results were obtained and are presented in this chapter along with the results of complementary atomic absorption studies performed as an independent means of verification.

B. Experimental

B-1. DLI Apparatus

The instrumental arrangement used in the DLI studies was essentially the same as that described in Chapter II except for the flame. For this the burner mount was modified to accommodate a slot burner taken from the atomic absorption unit used in the verification experiments. (Model AA5, Varian Techtron Pty. Ltd., Springvale, Australia). This burned a premixed air-acetylene flame. Sample introduction was accomplished with a pneumatic nebulizer driven by the air stream. Actual flame conditions are discussed in the forthcoming results section.

B-2. Atomic Absorption Apparatus

A commercial atomic absorption (AA) unit (Model AA5, Varian Techtron Pty. Ltd., Springvale, Australia) was used in all experiments performed to verify the results of the DLI studies of the well water and blood serum samples.

B-3. Reagents

The concentrated Ca stock solution used to make standard additions was made from reagent grade $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (J.T. Baker Chemical Co., Phillipsburg, NJ). This

solution had a nominal concentration of 10,000 $\mu\text{g/mL}$ Ca. Standardization with EDTA revealed an actual concentration of 9370 $\mu\text{g/mL}$.

All dilutions were made with distilled, deionized water.

B-4. Samples

The unsoftened well water sample was obtained from P. Wiegand. The blood serum sample was obtained from a commercial source (Moni-Trol ES Level II Chemistry Control and Carbonate Diluent II, Lot no. PTS-103, Diluent XSD2-132, American Dode, Miami, FL). This was reconstituted as suggested by the manufacturer.

B-5. Standard Additions Procedure

The standard additions method was chosen for the analyses to minimize the effects of physical and chemical interferences.

The well water sample was known to be approximately 100 $\mu\text{g/mL}$ Ca. Preliminary studies showed that both the AA and DLI instruments produced the best results when Ca concentrations in the range of 0.5 to 10 $\mu\text{g/mL}$ were used. Because of this, each of the solutions in the series made for the standard additions method was prepared by adding a 1 mL aliquot of the well water sample and a μL quantity (between 0 and 100 μL) of the stock solution to a 100 mL volumetric flask and diluting to the mark with distilled, deionized water. A description of this series of solutions

is given in Table 6-1. In this, X stands for the amount of Ca (in $\mu\text{g/mL}$) in the original well water sample divided by 100.

As with the well water samples, the blood serum samples were known to contain slightly more than 100 $\mu\text{g/mL}$ Ca. To make each of the solutions for the series in this case a 500 μL aliquot of the serum sample and a μL quantity of the stock solutions (between 0 and 50 μL) were added to a 50 mL volumetric flask and diluted to the mark with distilled, deionized water. A description of this series is given in Table 6-2. As before, X stands for the amount of Ca (in $\mu\text{g/mL}$) in the blood serum sample divided by 100.

Class A glassware was used for all solution preparation. The μL additions noted above were all made with automatic pipettes (Eppendorf, Brinkmann Instruments, Inc., Westburg, NY).

With the standard additions method the amount of analyte originally present in solution can be obtained by plotting the analytical signal versus the volume of stock solution added. The X-intercept of the plot then gives the negative of the number of μL that would have to be added to a "clean" sample to get the response given by the solution to which no addition was made. Concentration is then found with a simple calculation which also takes dilution factors into account.

TABLE 6-1. Solutions for Well Water Sample Experiments.

Sample Number	Standard Addition (μL)	Ca Concentrations ($\mu\text{g/mL}$)
1	0.0	X
2	10.0	0.937 + X
3	20.0	1.87 + X
4	30.0	2.81 + X
5	50.0	4.68 + X
6	100.0	9.37 + X

TABLE 6-2. Solutions for Blood Serum Sample Experiments.

Sample Number	Standard Addition (μL)	Ca Concentrations ($\mu\text{g/mL}$)
1	0	X
2	5	0.937 + X
3	15	2.81 + X
4	25	4.68 + X
5	50	9.37 + X

C. Results

C-1. Well Water Sample Analysis

In the DLI and AA experiments five replicate determinations were performed on the series of solutions described in the last section. The averaged DLI results are shown graphically in Figure 6-1. The plot is linear for solutions up to and including the 50 μ L addition. Because of this, a linear regression analysis was performed on the first four points in each data set. The x-intercept for each set was calculated in order to determine the Ca concentration of the original sample. The averaged results of the AA experiment are shown graphically in Figure 6-2. The same linear range is observed as in the DLI experiments. As before, a linear regression analysis was performed on each data set and the x-intercept in each case was calculated. A comparison of the results obtained with both methods is given in Table 6-3. The student "t" test shows that the difference between these means is not significant at the 95% confidence level.

C-2. Blood Serum Samples

The complex nature of the blood serum sample presented a difficult test for the DLI technique. This matrix contains high concentrations of easily thermally ionized components (e.g. the Na concentration alone is estimated to be approximately ten times greater than the Ca

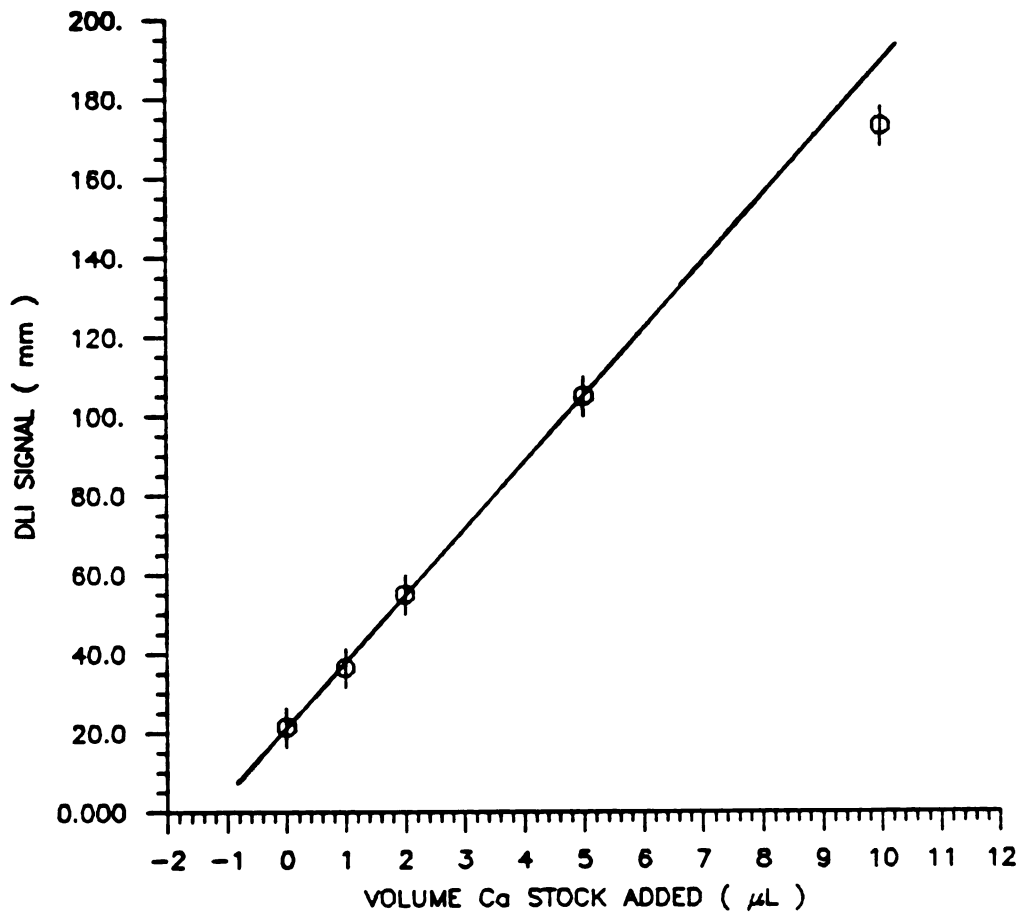


Figure 6-1. Standard additions analysis of Ca in well water sample (DLI).

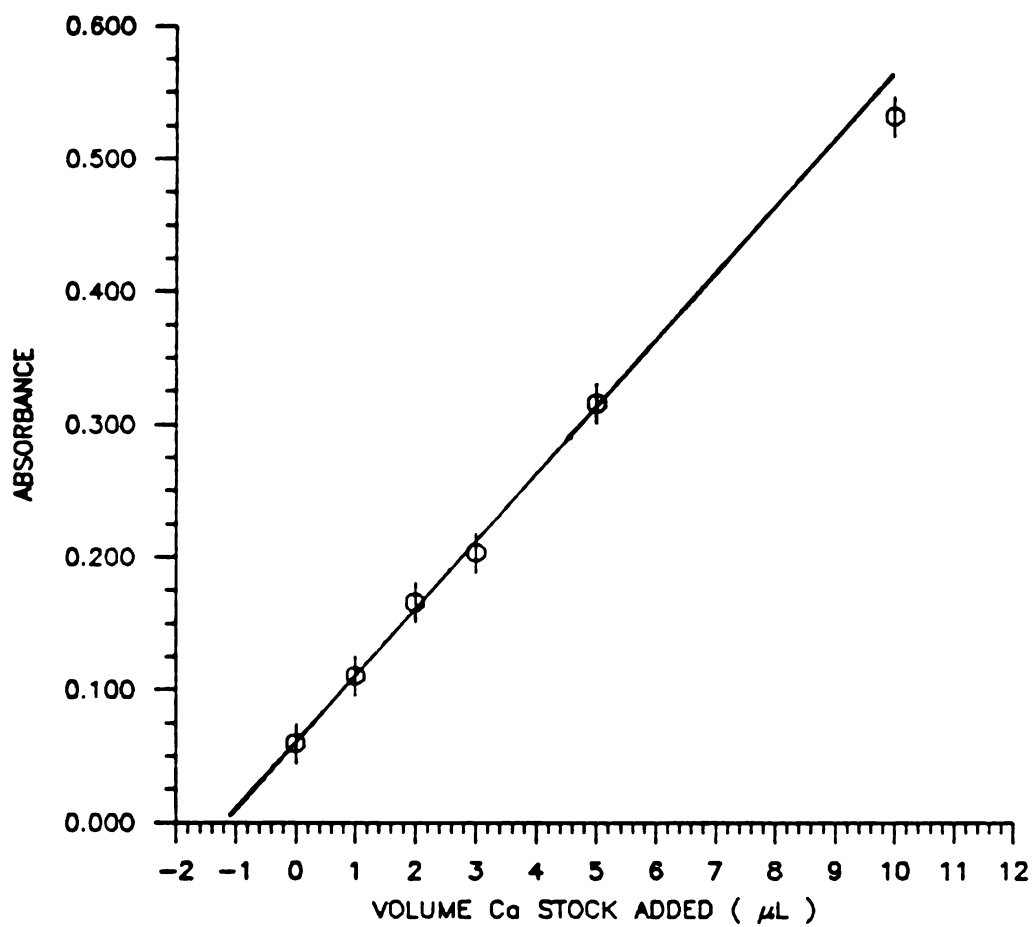


Figure 6-2. Standard additions analysis of Ca in well water sample (AA).

concentration). Preliminary results showed that the DLI signal was highly dependent on flame conditions. Optimal results were obtained when the flame was adjusted to burn in a slightly fuel-lean condition with a high air flow rate. This is probably caused by a number of factors. The air drives the nebulizer and so the higher rate means better sample nebulization. Also, excess O_2 in the flame leads to more complete combustion and a lessening of electrode fouling.

TABLE 6-3 Comparison of Results of DLI and AA Analysis of Ca in Well Water Sample

Method	Average X-intercept (μ L)	Average Value of Ca Concentration in Original Sample (μ g/mL)
DLI	12.3 ± 0.23	115 ± 2.2
AA	11.9 ± 0.21	112 ± 2.0

Five replicate DLI determinations were performed on the series of solutions. For graphical clarity, the results of only the first three trials are shown in Figure 6-3, the other two trials gave similar results and are discussed in the text. The figure shows that the signal dropped steadily as the experiment progressed. The signals obtained in the fourth and fifth trials, however, were slightly larger than those found in the third. This

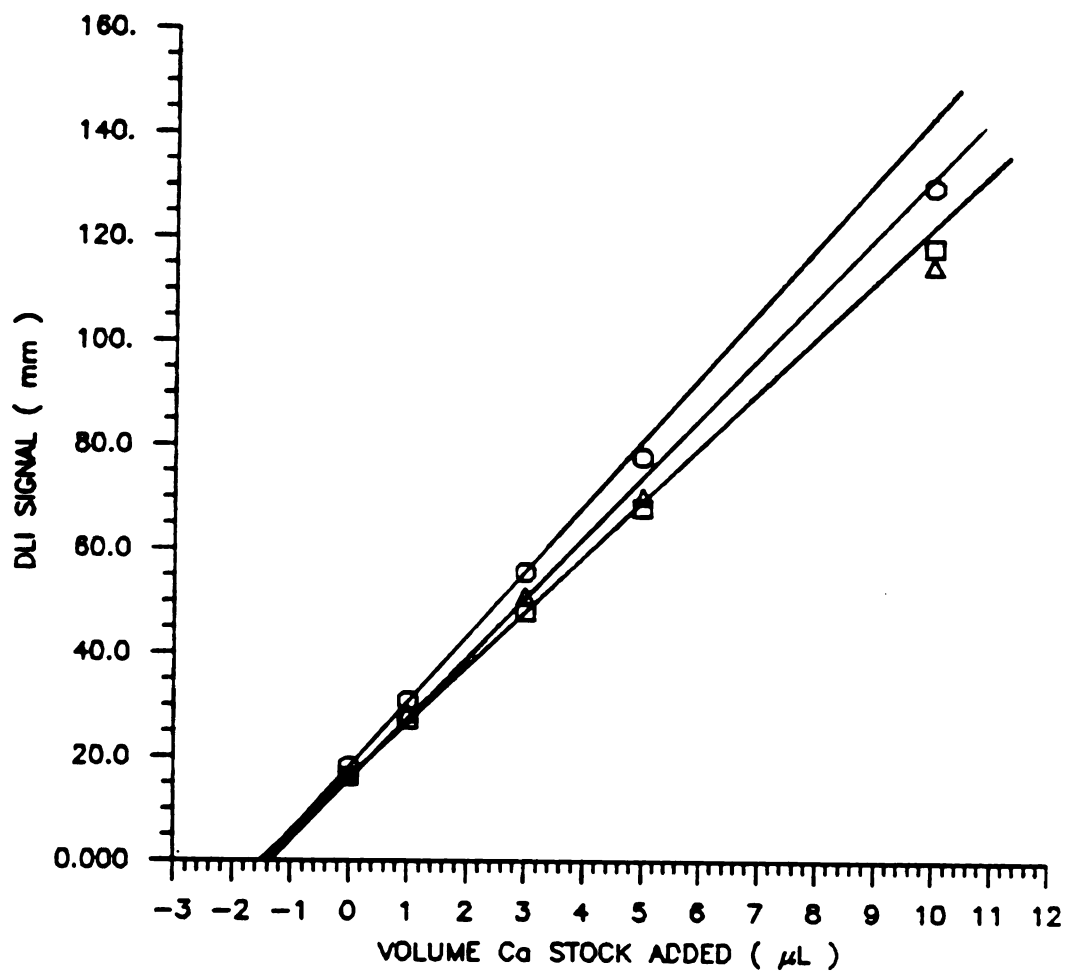


Figure 6-3. Standard additions analysis of Ca in blood serum sample (DLI). ($\circ$) trial 1; (Δ) trial 2; ($\square$) trial 3.

behavior is probably caused by electrode fouling. In earlier experiments blood serum samples were found to deposit carbon on the electrodes. These deposits can influence the electric field between the probes and decrease the collection efficiency. Before beginning the experiments described herein the electrodes were sanded clean. Carbon deposits were seen to form during the experiments. Also particulates were observed to dislodge from the probes the course of the experiments. This probably explains the slight increase in signal described above. In any event, the signal was seen to deviate from linearity after the third point so only the first three points in each data set were used in the regression analysis to find the x-intercept and thus the Ca concentration in the original sample. The results are reported in Table 6-4.

TABLE 6-4. Comparison of Results of DLI and AA Analysis of Ca in Blood Serum Sample

Method	Average X-intercept (μL)	Average Value of Ca Concentration in Original Sample ($\mu\text{g/mL}$)
DLI	14.5 ± 0.75	136 ± 7.0
AA ¹	14.9 ± 0.40	140 ± 3.8
AA ²	14.4 ± 0.71	135 ± 6.7
¹ air-acetylene flame		
² nitrous oxide-acetylene flame		

Complementary AA experiments were performed with both a nitrous oxide-acetylene flame and the air-acetylene flame. The experiment was performed nine times with the air-acetylene flame, and the averaged data are shown in Figure 6-4 along with the averaged results of four replicates taken using the nitrous oxide-acetylene flame. If any serious chemical interferences were biasing the results obtained with the air-acetylene flame different results would be expected with the nitrous oxide-acetylene flame. The figure shows that this is not the case. While the absorbance values obtained using the nitrous oxide-acetylene flame were higher than those obtained using the air-acetylene flame, due to the higher atomization efficiency in the nitrous oxide-acetylene flame, the x-intercepts (which translate to the sample concentrations) are nearly identical. The results of both of the AA analyses are given along with the DLI results in Table 6-4. The student "t" test shows that the differences between the means given in the table are not statistically significant at the 95% confidence level. Thus the two methods produce essentially equivalent results.

The value of the Ca concentration in the reconstituted blood serum sample reported by the supplier is 127 ± 2 $\mu\text{g/mL}$ Ca. This value was obtained by a well-established method (in this case AA). Other methods yielded results from 113 to 138 $\mu\text{g/mL}$. Thus the values obtained herein lie

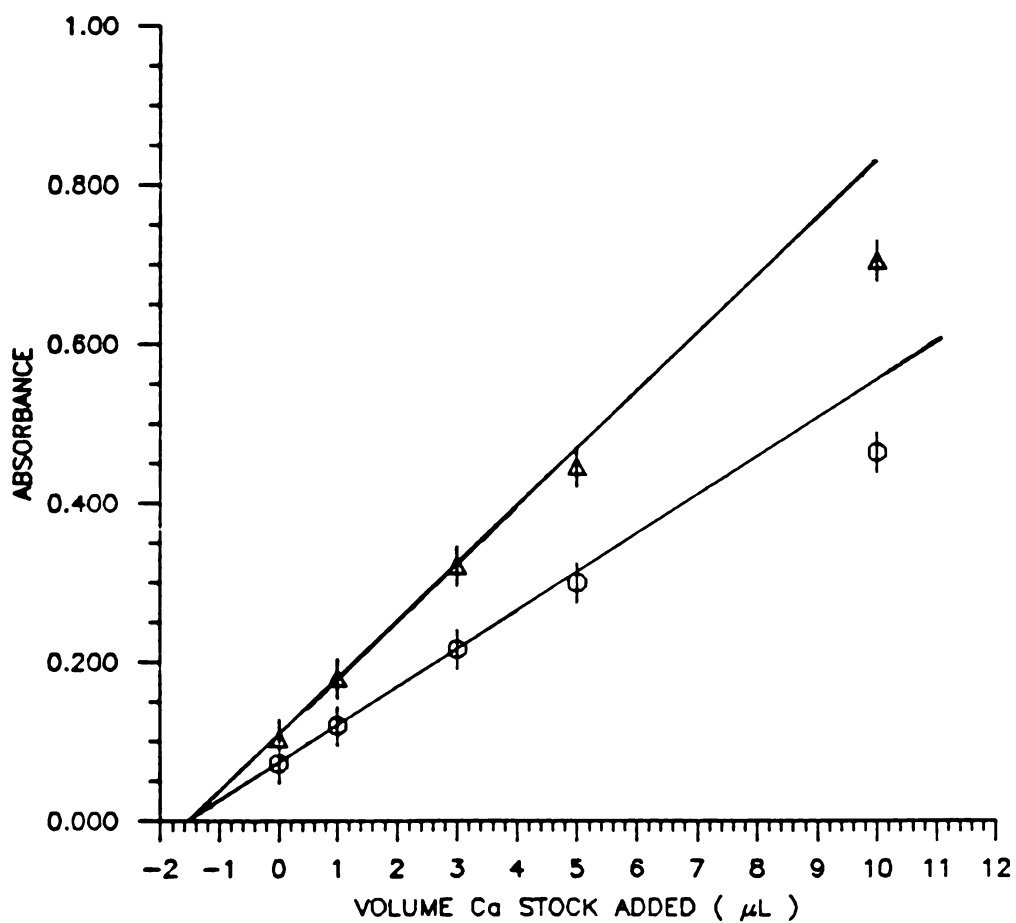


Figure 6-4. Standard additions analysis of Ca in blood serum sample (AA). (Δ) nitrous oxide-acetylene flame; ($\bigcirc$) air-acetylene flame.

on the high side of the expected range. The consistency between the AA and the DLI results suggests that this discrepancy is due to some systematic error, such as a slight miscalibration in the automatic pipette or the standard solution, rather than any fundamental limitation of the DLI technique.

CHAPTER VII

SUMMARY AND FUTURE DIRECTIONS

A. Summary

Four aspects of DLI have been examined in the preceding chapters in order to characterize the basic processes involved in the technique and to illustrate its potential as a useful analytical method.

First, the energetics of the various processes which affect signal generation in the DLI experiment were studied (Chapter III). Basic ionization pathways in laser atomic flame spectroscopy were examined both from a theoretical and from an experimental standpoint. The photoionization pathway was found to dominate under the proper conditions, the most important being a close match between the energy defect and the photon energy of the ionizing laser beam. Various optimization strategies were then presented based upon this result.

The next chapter treated the dependence of ionization signals upon laser power in both LEI and DLI. Dye laser power dependencies in single photon resonant and non-resonant LEI and in two photon LEI were examined. Similar studies were described for resonant DLI and the signal

dependence on ionizing beam power was studied and discussed. The most important results indicated that the DLI signal was not saturated with respect to ionizing beam power and that the actual area from which a majority of the ionization signal arises is quite small.

A search for ionization interferences in the DLI technique was detailed in Chapter V. The major contributor to signal degradation was found to be the formation of a charge sheath around the ion-collecting cathode. This sheath essentially negates the potential difference between the probes and was found to be most severe when easily ionized components were contained in the sample matrix. Minimization of the interference was shown to be possible by keeping the ionization region close to the cathode (i.e. within the boundary of the sheath). Off-resonant photoionization of matrix components as well as some chemical interferences were also discussed.

Finally, analytical applications of the DLI technique were examined in Chapter VI. Here an air-acetylene flame was used for the first time in the DLI experiment. Several experiments were described in which various sample matrices were tested for calcium content. The results were consistent with those obtained by other means.

The DLI technique has a promising future as a sensitive and selective technique for the analysis of trace metals in flames and also as a tool in combustion diagnostics. There are many areas in which further study should

improve both the fundamental understanding and the general utility of the technique. Some of these are discussed in the next section.

B. Future Directions

Although the nitrogen pumped dye laser system was a good starting point it is clear that a different laser system could improve the DLI technique substantially. The present system suffers from three major shortcomings. First, there is not enough power in the dye laser beam to allow frequency doubling. This means that the ultraviolet wavelengths necessary for the study of high ionization potential elements are inaccessible. Although the power output of the present dye laser could probably be significantly improved by replacing the grating now in use with one having a more optimal blaze angle, it is doubtful that a reliable frequency doubled beam of reasonable power could be obtained in a convenient and inexpensive fashion. The single fixed wavelength at limited power in the ionizing laser beam is also a drawback. Finally, the radio frequency noise generated by the breakdown of the spark gap in the nitrogen laser is a major limitation as it prevents the examination of very rapid signals.

The Nd:YAG pumped system available in the departmental laser facility would be an excellent choice as a replacement. It has a number of advantages over the present

system. First, the dye laser can be frequency doubled to provide an ultraviolet excitation beam. For preliminary studies a moderate amount of selectibility in the choice of ionizing wavelength could be derived by simply doubling, tripling or quadrupling the infrared fundamental (1064 Å). The non-linear crystals necessary for this are already available so the experimenter could choose between 532 nm, 355 nm and 266 nm (2.33 eV, 3.49 eV and 4.66 eV, respectively). As an example, Ni could be used as the analyte in initial studies. It has a strong resonant transition at 232 nm (oscillator strength, $f = 0.68$) which could be reached by frequency doubling the output of the strong, blue Coumarin 460 laser dye. The energy of overshoot (see Chapter III) with a 532 nm ionizing beam would be only 0.04 eV. As this is extremely close to threshold a reasonable DLI signal would be expected.

If preliminary experiments such as the one described above are successful, the experiment could then be expanded by assembling a second dye laser to provide a truly tunable ionizing source. This would make possible a number of experiments. First, optimization of analytical signals would be possible. In addition, the relative magnitudes of cross-sections for ionization with respect to the photon energy (wavelength) in the ionizing beam could be obtained and compared to values from theoretical calculations. Population redistribution upon laser excitation could be studied using electrical detection

once confidence in cross-section values was obtained. This would eliminate the experimental complexities of fluorescence detection which are presently involved in this type of experiment.

The inherent spatial resolution available through the use of crossed, rather than colinear, beams can be put to use in combustion diagnostics. With proper focusing and alignment the region from which the majority of the ionization signal arises could easily be made to be as small as one cubic millimeter. A stationary probe/laser configuration in conjunction with a movable flame could easily be used to map atom distribution or flame temperature in three dimensions. As there are now many motorized positioning mounts available commercially, this type of experiment could be placed under complete computer control.

The analytical utility of the technique has barely been explored. In addition to enabling the study of high ionization potential elements, the move to the Nd:YAG laser system should greatly improve sensitivity. The reasons for this are two-fold. First, the power available for use in the ionizing beam will be higher than that available with the nitrogen laser system. As the ionization signal has been found to be linear with ionizing beam power, absolute signal magnitudes should increase. Secondly, the fact that the Nd:YAG rods are flashlamp

pumped will eliminate many of the noise problems related to the nitrogen laser spark gap.

Finally, the use of off-resonant transitions in the DLI process could prove to be an important and interesting area of study. The large LEI signal obtained from an obscure, off-resonant Ca transition, as detailed in Chapter III, at least justifies further study as many elements have strong transitions originating from low lying excited states. The selectivity of the technique could be greatly enhanced if reasonable signals could be obtained from these. A particularly interesting case for study is the Fe transition at 227.7 nm. The oscillator strength for this transition is about 2 and this is approximately four times larger than that of the major analytical line at 248.8 nm. A comparison of the DLI signals from these lines should prove quite informative.

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APPENDICES

APPENDIX A

APPENDIX A

TWO-STEP LASER ASSISTED IONIZATION OF SODIUM IN A HYDROGEN-OXYGEN-ARGON FLAME*

A. Introduction

Laser enhanced ionization (LEI) in flames and plasmas has been observed with various experimental designs^{6,21,68,128-132}. In the usual LEI experiment, ionization results from the absorption of a resonant laser photon followed presumably by collisions of the excited atom with flame gas combustion products^{6,68}. Absorption of a resonant laser photon with an energy E reduces the effective ionization energy and increases the ionization rate^{6,68} by a factor of $\exp(E/kT)$, where T is the flame temperature; this factor can easily be on the order of 10^4 . In this paper we report a relatively simple and inexpensive method for producing laser-assisted ionization in a flame. The method utilizes a two-step process, as suggested by various authors^{83,133}. The first step is the absorption of a resonant laser photon by an atom in the ground state, followed by the absorption of an off-resonant photon by the atom in the excited state. The sum of the energies of

the two photons is such that it exceeds the ionization energy of the atom.

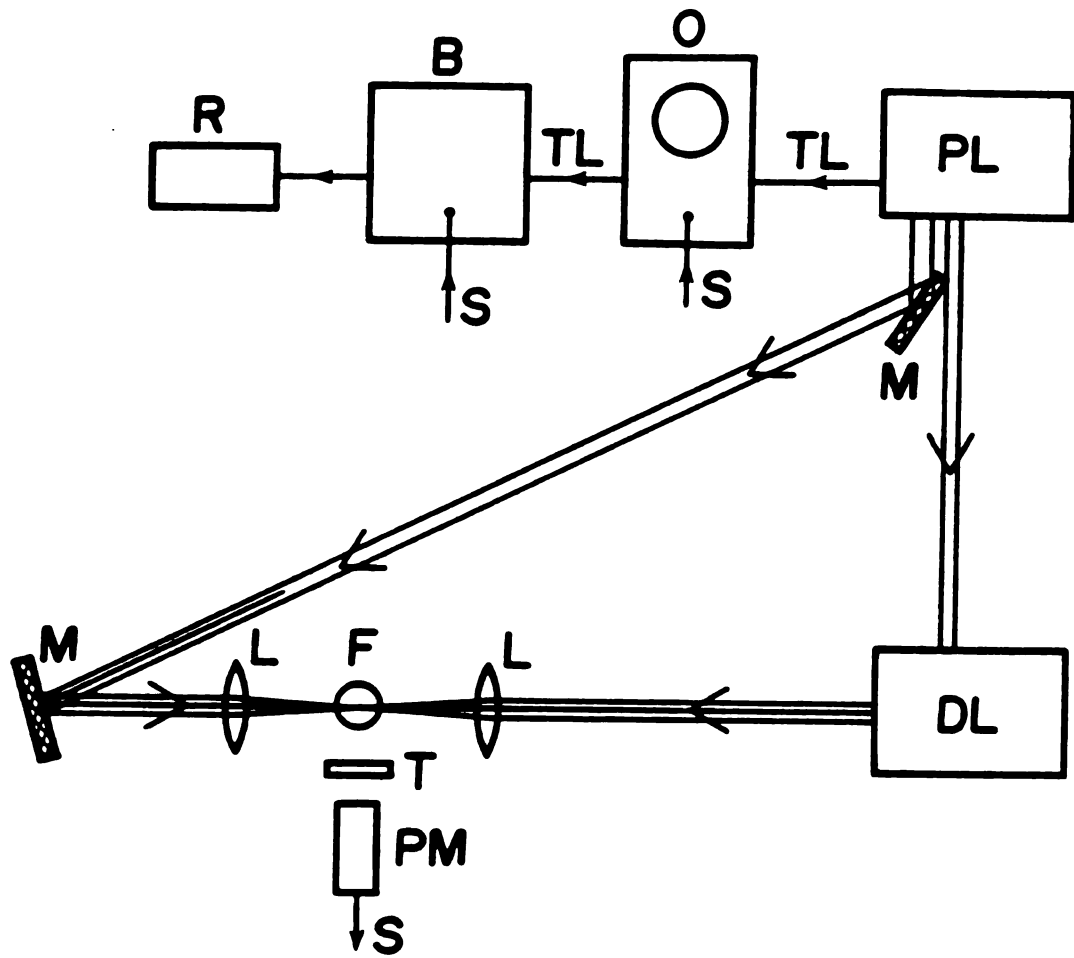
The fact that two laser photons are being used to ionize the atom does not necessarily mean that the ionization proceeds through a straightforward two-step process. It has recently been proposed that photoionization might be collision assisted¹³⁴. Since collisions are frequent in a flame at atmospheric pressure, this latter possibility was investigated, and some experiments are presented to elucidate the predominant ionization mechanism.

B. Experimental

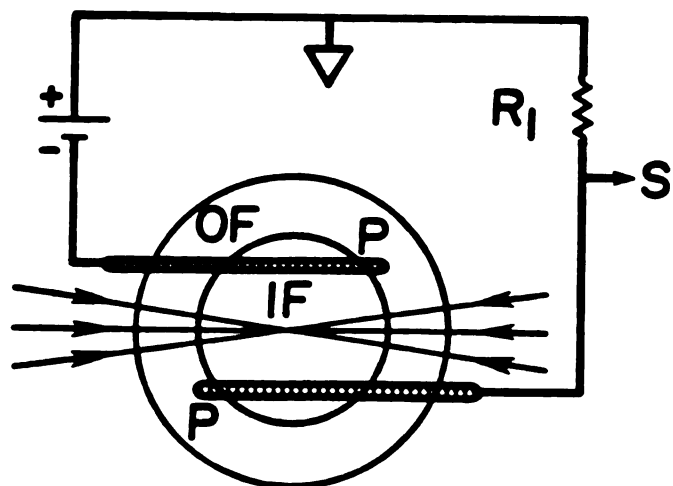
The experimental set-up is shown in Fig. A-1. A relatively cool (~ 1800 K) H_2-O_2 -Ar flame is burned from a circular Meker burner and shielded by a mantle flame of the same composition to prevent the entrainment of air. Sodium is introduced into the inner flame by nebulizing a sodium salt solution with a pneumatic nebulizer driven by the argon stream. A homemade tunable dye laser of the Hansch design⁹³, using Rhodamine 6G as a dye, is pumped by a N_2 -laser (Model 0.5-150, NRG, Inc., Madison, WI). The pulse duration is ≈ 5 ns for both lasers. The dye laser beam is focused in the center of the flame, approximately 2 cm above the burner head, well away from the combustion region. The width of the spectral profile of the dye laser at wavelength of $5890 \text{ \AA}$ was measured using the fluorescence excitation profile as discussed by Omenetto,

Figure A-1. Experimental arrangement for simultaneous observation of laser assisted ionization and laser induced fluorescence. a) Overall view. B, boxcar; D1, dye laser; F, flame, L, lens; M, mirror, O, oscilloscope; PL, pump laser; PM, photomultiplier, R, x-t recorder, S, signal; T, uv rejecting filter, TL, trigger line. b) Detailed view of probes and laser beams. IF, inner flame; OF, outer flame; P, probe; R_L , load resistor, S, signal. Dimensions are not to scale. The waist diameter of the laser beams is of the order of 0.1 mm; the distance between the probes is a few mm; the diameter of the inner flame is approximately 15 mm.

a.)



b.)



et al.¹³⁵ and found to be $(0.7 \pm 0.1) \text{ \AA}$. The wavelength of the N_2 laser is 337 nm. Output powers were measured with a pyroelectric power meter (Model J3-05, Molelectron Corp., Sunnyvale CA). Part of the N_2 laser beam was split off from the pumping beam and also directed into the flame, where it was focused with a quartz lens. Positioning devices carrying mirrors and lenses facilitate in maximizing the spatial overlap of the two laser beams. The degree of temporal overlap between the two laser pulses can be varied by changing the optical path lengths of one or both lasers. The path lengths were adjusted in these experiments for maximum temporal overlap of the two lasers at the burner.

The ionization signal was detected with a pair of biased nichrome wires, which had a diameter of 0.7 mm. These probes were mounted on micrometer-driven translation stages and located in the immediate neighborhood of the irradiated region, but were not irradiated themselves. Ionization signals were measured across an interchangeable load resistor in the probe circuit. The signals from the probes were usually processed by a boxcar averager with gated integrator (Model 162-164, Princeton Applied Research, Princeton, NJ) and read out by an x-t recorder. A photomultiplier (RCA 1P28) wired for fast pulse processing monitored the fluorescence from the 3P-3S transitions of sodium. Both the ionization and the fluorescence signal can be observed on a storage oscilloscope (model 564

Tektronix, Inc., Beaverton, OR). Appropriate shielding prevents stray light due to the dye laser from entering the photomultiplier. A UV rejecting filter in front of the photomultiplier was used to cut out stray light due to the N_2 -laser. Two r.f. chokes, consisting of several wire turns around a ferrite core, were soldered into the H.V. power line of the N_2 -laser; both the laser and the chokes were put inside a grounded Faraday cage, consisting of 0.5 mm copper plating. These measures substantially decreased the r.f. noise from the N_2 -laser discharge.

C. Results and Discussion

Experiments were performed to measure the enhancement of the ionization signal with both the dye laser and the N_2 laser irradiating the flame over the signal obtained with dye laser alone. For these experiments, the dye laser was tuned to the $Na(3S_{1/2} \rightarrow 3P_{3/2})$ transition and a Na concentration of 12 $\mu\text{g/ml}$ was nebulized into the flame. The laser peak powers were of the order of 40 kW and 100 kW for the dye laser and the split off part of the N_2 laser beam, respectively. The ionization signal was integrated over time. With the dye laser only, an ionization signal of 9.0 mV was obtained; with both lasers the ionization signal increased to 1.3 V. No signal was obtained with the N_2 laser alone. The enhancement factor was thus 144 for these experiments. The exact enhancement factor depends on the configuration of the beams and the probes,

the intensities of the beams and the composition of the flame. We observed that this factor can be improved by moving the probes closer to the irradiated region. The latter manipulation, however, tends to affect the reproducibility of the experiment because of the more critical alignment. Moreover, when the lasers irradiate probe surfaces, non-specific ionization occurs, which is possibly due to electrons being liberated from the probe material by laser photons or due to off-resonant multiphoton ionization of atoms and molecules in particle sheaths which might envelop the probes.

To investigate the analytical utility of the two-step ionization technique, the ionization signal and the degree of ionization were measured as a function of the sodium solution concentration. The results are given in Fig. A-2. The dye laser was tuned to the $\text{Na}(3S_{1/2} \rightarrow 3P_{3/2})$ transition, the N_2 laser irradiated the same flame volume, and the time-integrated ionization signal was measured. The analytical curve shows a nearly constant slope of one over more than two decades of solution concentration, and the lowest concentration detected was $0.1 \mu\text{g/ml}$. From the fact that a slope of one occurs it can be concluded that associative ionization is not present to any significant extent, since two sodium atoms are required ($2\text{Na}^* + h\nu \rightarrow \text{Na}_2^+ + e^-$ ^{136,137}) and a slope of two would result. The non-linearity of the curve in Fig. A-2 may be due to a

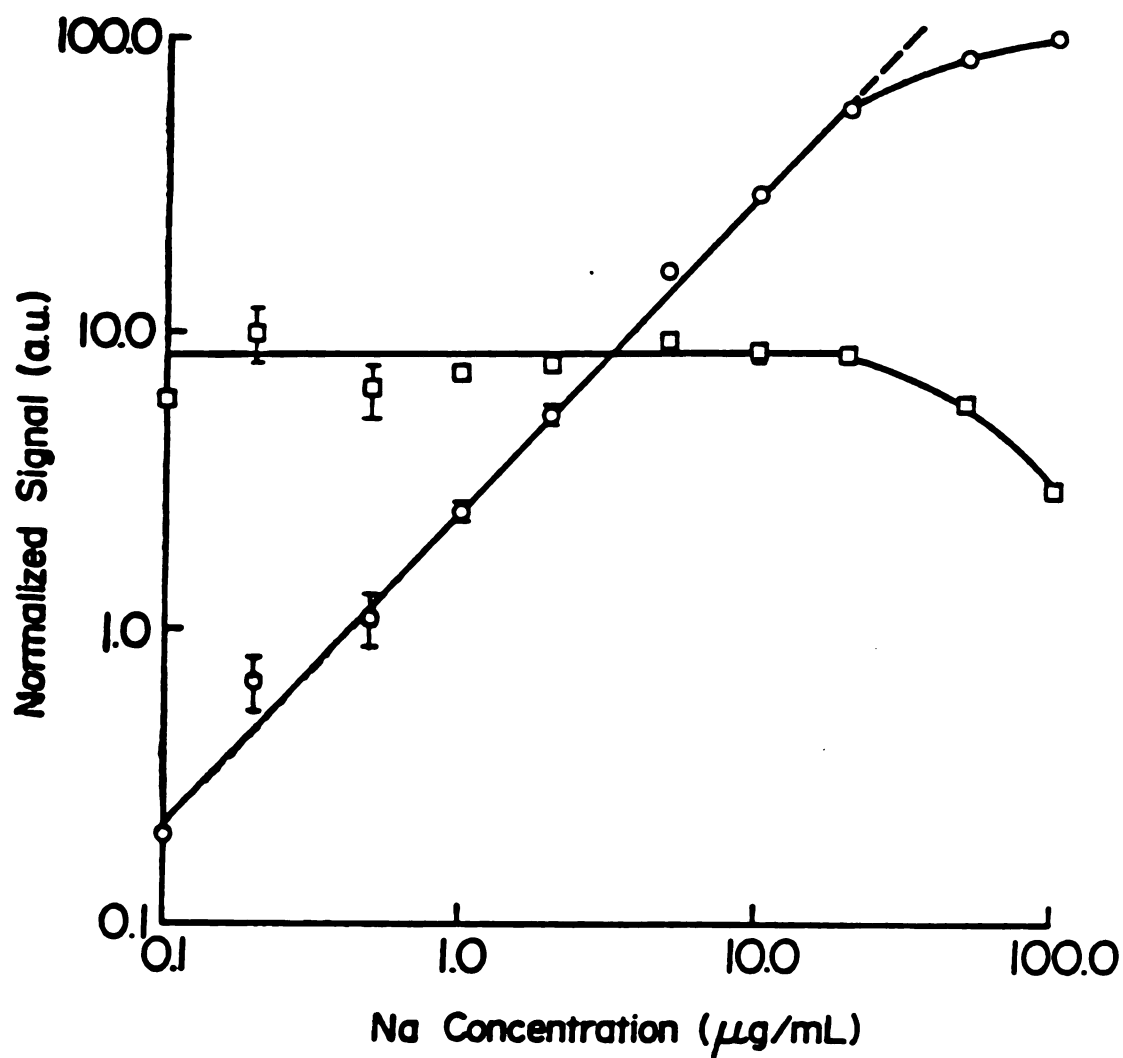


Figure A-2. Ionization signal (○) and ratio of ionization signal to sodium solution concentration (□) vs. sodium solution concentration; both lasers are irradiating the probed volume. The dye laser was tuned to the $3S_{1/2} \rightarrow 3P_{3/2}$ (589.0 nm) transition.

decrease in the ion collection efficiency caused by the formation of charge sheaths¹³ or by ion-electron recombination.

A plot of the ratio of the ionization signal to the sodium solution concentration versus the sodium concentration has been previously related to the degree of ionization⁶. Such a plot, shown in Fig. A-2, also exhibits non-linearity. This phenomenon has been observed with a different ionization scheme, but in virtually the same flame⁶. That the deviation from linearity in Fig. A-2 was not due to nebulizer characteristics was checked by plotting the thermal emission from the $\text{Na}(3P \rightarrow 3S)$ transitions against sodium solution concentration. The latter plot showed deviations from linearity in a concentration range well above that of Fig. A-2, due to the combined effect of self absorption and decreasing atomization efficiency with increasing concentration.

Profiles of the ionization- and fluorescence signal were obtained by tuning the dye laser across the $\text{Na}(3S_{1/2} \rightarrow 3P_{3/2})$ transition, and are shown in Fig. A-3. The sodium solution concentration nebulized into the flame was 12 $\mu\text{g/ml}$. The difference in the full widths at half maximum (FWHM) which is evident from the profiles of Fig. A-3, has been observed in a related experiment by van Dijk, et al.⁶ where a flashlamp laser was used.

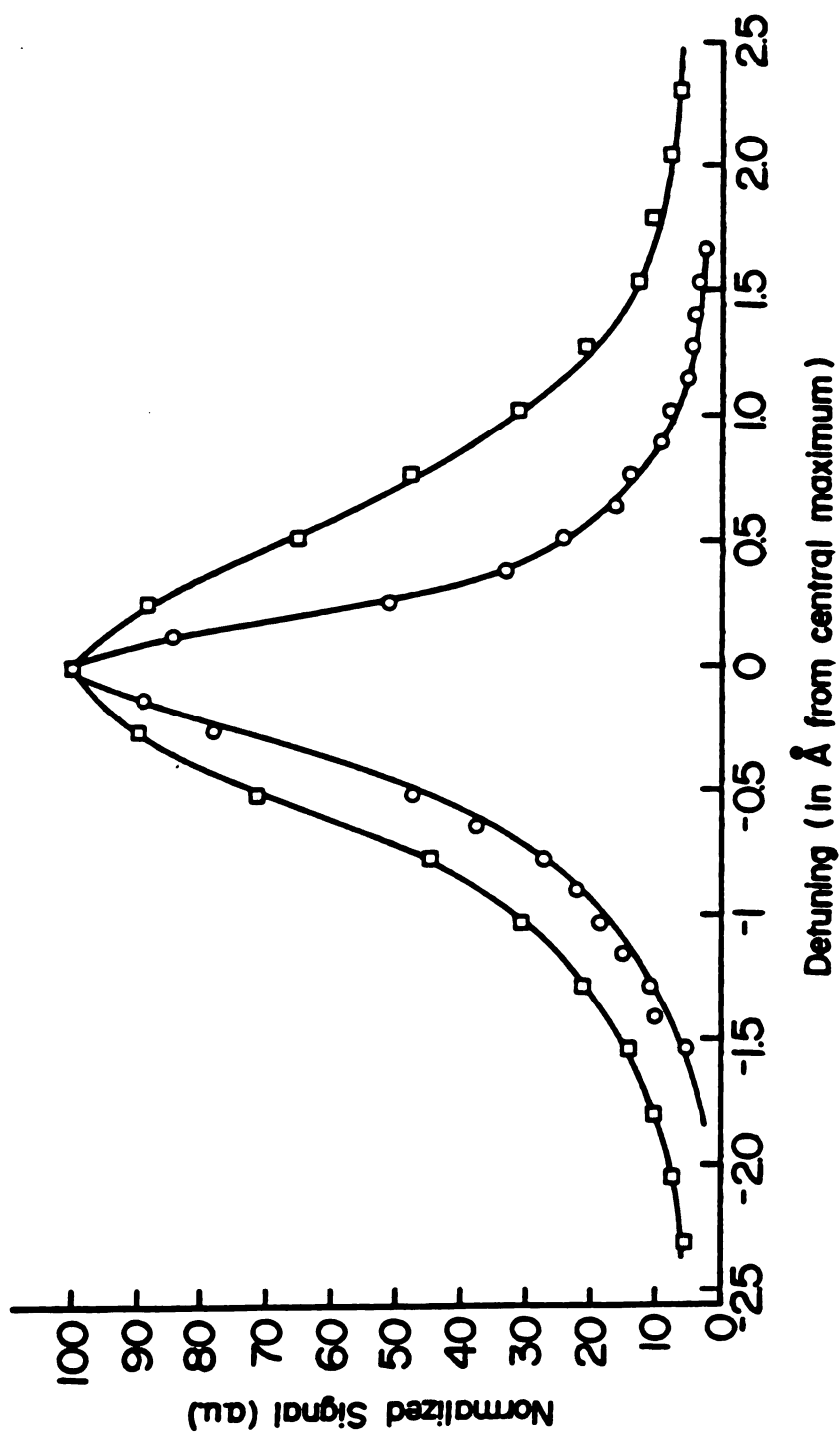


Figure A-3. Profile of ionization signal ($\square$) and fluorescence signal ($\circ$) obtained by scanning dye laser across the $3S_{1/2}$ to $3P_{3/2}$ (589.0 nm) Na transition. FWHM = 0.7 Å for fluorescence profile and 1.5 Å for ionization profile. Sodium solution concentration = 12 $\mu\text{g/mL}$, probe voltage = 400 V.

The fluorescence excitation profile in Fig. A-3 essentially represents the spectral laser profile because the width of the $\text{Na}(3P \rightarrow 3S)$ transitions is known to be approximately $70 \text{ m}\text{\AA}$ in our flame¹³⁸, which is small compared to the observed width. Saturation of the $\text{Na}(3P_{1/2} \rightarrow 3P_{3/2})$ transition hardly affects the latter conclusion, since the broadening of the excitation profile depends on the square root of the natural logarithm of the dye laser power¹³⁵ and is therefore a weak function of this power. The measured FWHM of $0.7 \text{ \AA}$ of the fluorescence excitation profile is consistent with the value which we obtained when using a monochromator to resolve the spectral laser profile. Broadening of the ionization profile might be related to saturation of the laser-excited level, space charge effects¹³, and possibly recombination⁶.

On a μs time scale the onset of the recombination might occur and this might partially account for the difference in widths observed in the profiles of Fig. A-3⁶. As noted by Muller, et al.¹³⁹, appreciable charge densities are needed to give rise to noticeable recombination on a μs time scale. We offer the following hypothesis to account for recombination under our experimental conditions: the possible existence of charge sheaths around the probes might partially nullify the electric field between the probes and lead to an increase in the contribution of diffusion to the motion of the charges in the

'field-free' region. Therefore, a significant number of ions might be able to overcome the repulsive field at the positive probe. These ions have a higher probability of being neutralized because of the electron sheath enveloping the latter probe. An analogous reasoning applies to the electrons. As the charge densities in the sheath are higher than in the surrounding plasma, the recombination rate will also be higher near the sheaths. The fact that space charges diminish the field might also decrease the collection efficiency of the probes and give rise to broadening of the ionization profile.

We investigated the dependence of the ionization and fluorescence signals on small variations in flame gas composition. The influence of changing the oxygen content on the signals is quite noticeable, but different for the excited state population and the ionization. However, the *ratio* of the ionization signal to the fluorescence signal shows only a weak dependence on the O_2 concentration. The ratio of the ionization signal to the fluorescence signal is proportional to the degree of ionization β , provided β is small and the $3S_{1/2} \rightarrow 3P_{3/2}$ transition is saturated.

$$\beta \equiv [Na^+]/([Na^+] + [Na]) \approx [Na^+]/[Na^*] \propto i/F \quad (1)$$

where $[Na^*]$ is the density of the excited sodium atoms;
 i = ionization signal and F = fluorescence signal.

In an analogous experiment, where we varied the argon content of the flame, a similar weak dependence was observed, as is evident from the curves in Fig. A-4. From these experiments one can conclude that if the degree of ionization is low, the discrete to continuum step is predominately photon absorption and thus affected only slightly by collisions with O_2 or Ar. On the other hand, if the degree of ionization β is high, this conclusion does not necessarily hold because a variation in the ionization rate will have little influence on β for β close to unity. Rough calculations indicate that the degree of ionization within the laser irradiated volume may indeed be quite high. When the discrete to continuum step is brought about solely by collisions, the dependence of i/F on the O_2 concentration in the flame is much more pronounced^{6,124}.

Changing the voltage across the probes results in a change of ionization signal, as is shown in Fig. A-5. For this experiment we used various sodium solution concentrations, and the dye laser was tuned to the $3S_{1/2}$ to $3P_{3/2}$ transition. With increasing voltage the curves are seen to level off, especially those of the higher concentrations. The decreasing slopes indicate that the current drawn from the plasma approaches saturation, which means that with high voltages eventually all the available charge carriers in the probed region are being collected.

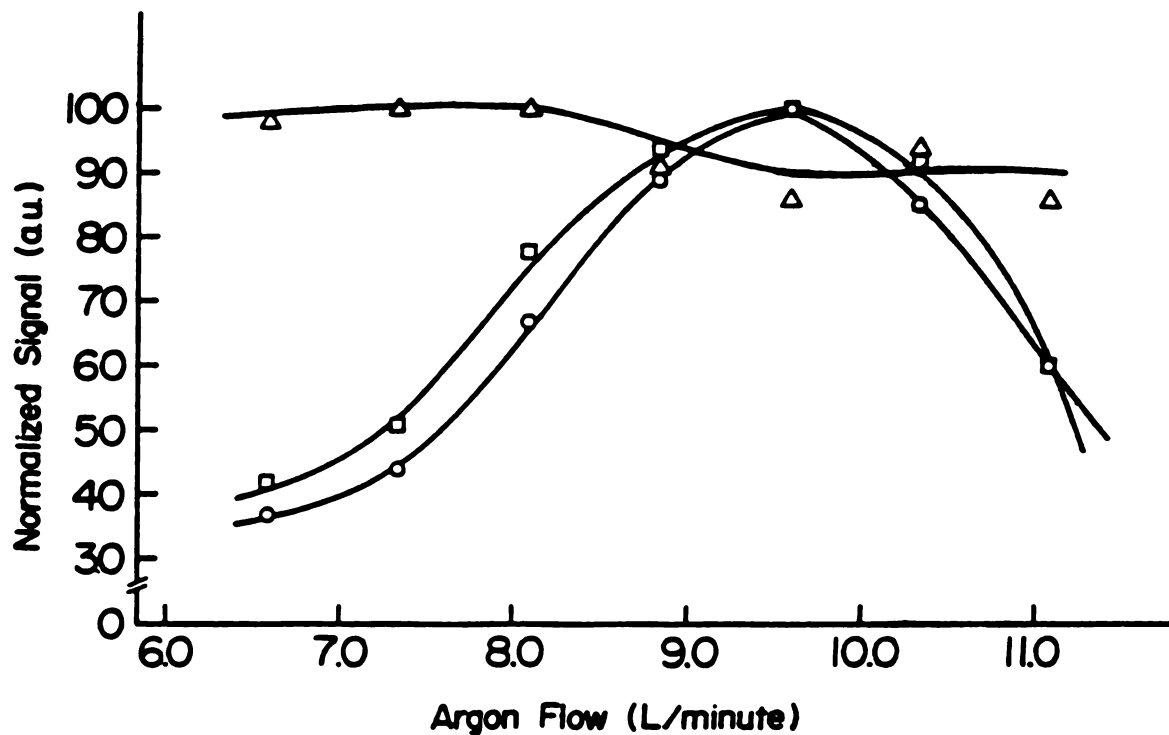


Figure A-4. Dependence of ionization and fluorescence signals on Ar content of flame. The dye laser was tuned to $\text{Na}(3S_{1/2} \rightarrow 3P_{3/2})$ transition; the sodium concentration was 12 g/ml. (○) fluorescence signal plotted vs. Ar flow; (□) ionization signal plotted vs. Ar flow; (Δ) ratio of ionization-to-fluorescence signal plotted vs. Ar flow.

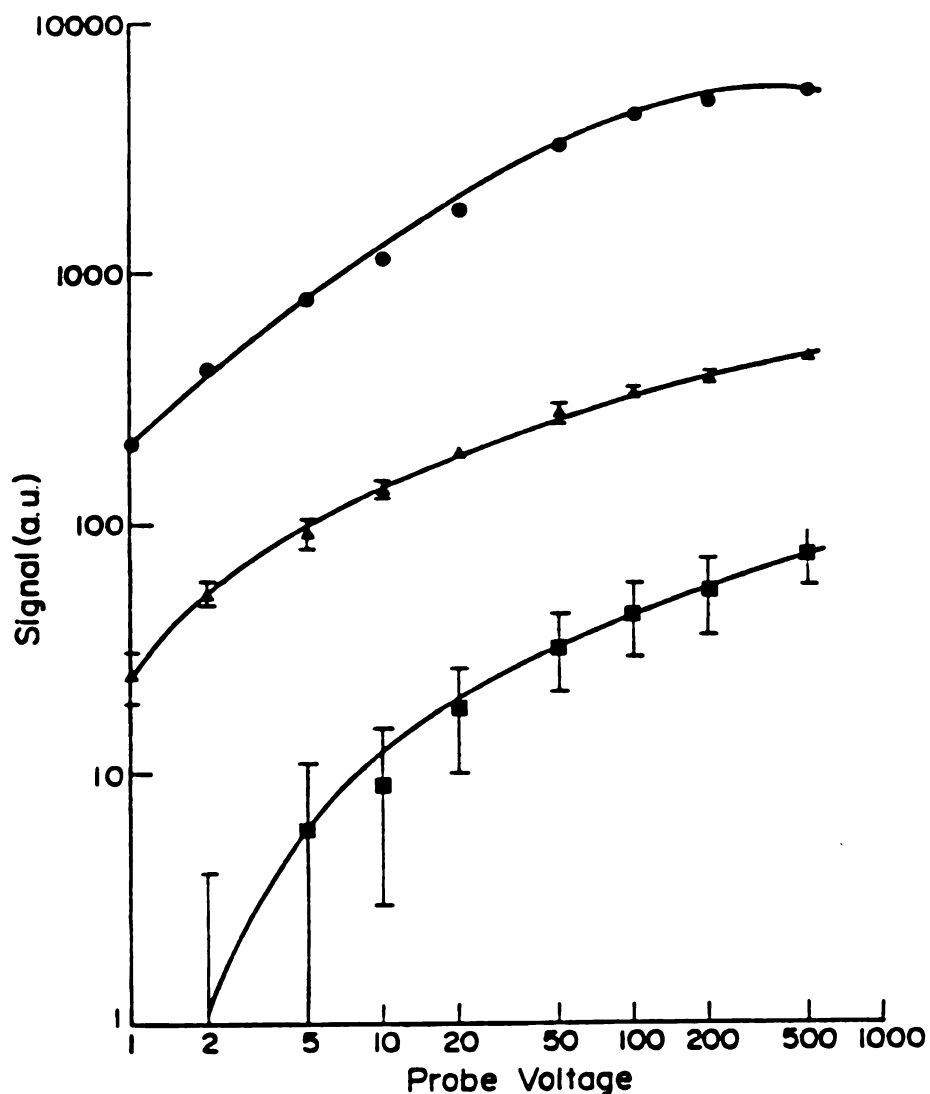


Figure A-5. Dependence of ionization signal on probe voltage for various sodium solution concentrations. The dye laser was tuned to the $3S_{1/2} \rightarrow 3P_{3/2}$ transition. A dc component in the signal, probably due to thermal (non-laser) ionization, was eliminated with a capacitor in the signal line. (●) sodium concentration = 10 ppm; (▲) sodium concentration = 1 ppm; (■) sodium concentration = 100 ppb.

A check as to the transport mechanism can be obtained by plotting the measured decay time τ of the ionization signal versus the reciprocal of the applied probe voltage $2\phi_p$. According to eqn. (A13) of the appendix, such a plot is expected to yield a straight line: indeed we found this to be the case. From the slope of this plot we calculate, using eqn. (A13) with $2L = 2.8$ mm, that the ionic mobility μ_i is on the order of $20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. When we assume that the additional decay time τ_e introduced by the circuitry, especially the load-resistor ($= 100 \text{ k}\Omega$), is simply added to the characteristic decay time τ_i , we find from the intercept of the plot of decay time versus inverse probe voltage that $\tau_e = 20 \text{ }\mu\text{s}$. Hence the stray capacitance of the circuitry is $\sim 200 \text{ pF}$, in reasonable agreement with estimates based on cable length and input capacitance of the apparatus.

Using the relation $\mu_i = qD/(kT)$, where q = elementary charge, D = diffusion coefficient, k = Boltzmann's constant and T = flame temperature, we calculated the order of magnitude of μ_i from measurements of the diffusion coefficient in flames by Ashton and Hayhurst¹⁴⁰ and found our result to be within the range of the latter authors. Electronic mobilities are expected to be much larger because of the difference in mass between the ions and the electrons¹⁴¹. When we calculate the decay time under the assumption that diffusion is the predominant transport mode, we find, using $\tau_{\text{diff}} = (2L/\pi)^2/D$ ¹⁴², and

$D = \mu_i kT/q$, τ_{diff} is of the order of several milliseconds and is therefore much larger than our observed values. Two conclusions pertaining to the particular conditions of our experiment can be drawn from these experiments:

1. The predominant transport mechanism is drift due to the electric field of the probes.
2. The current is limited by the ions.

It follows from our measurements and from eqn. (A13) that the actual decay time of the charge cloud is several microseconds. In order to eliminate the contribution of the circuitry to the decay time constant, we plotted this contrast vs. the value of the load resistor. These latter measurements support our observation that τ_1 is of the order of a few μs , since for low values of R_ℓ the observed time constant becomes independent of R_ℓ .

The temporal dependence of the ionization signal was measured with a load resistor R_ℓ of 5 k Ω . The peak amplitude V_0 of this signal was 12 mV and the decay was close to exponential with a time constant τ of $7.9 \pm 0.2 \mu s$. An estimate of the total number N of ions collected in this pulse follows from

$$V_0 \int_0^{\infty} e^{-t/\tau} dt = NqR_\ell \quad (2)$$

where q is the elementary charge. From these results N is found to be approximately 10^8 . Note that the exponential

decay is consistent with eqn. (A4) of the appendix.

By tuning the dye laser across the 3S-4D two-photon transition of sodium and using a 100 $\mu\text{g/ml}$ sodium solution concentration, the profile shown in Fig. 6 was obtained. The signal from this transition is weaker than the signal of a 3P-3S transition when referred to the same solution concentration. The peak observed with the dye laser only is probably due to collisional ionization proceeding from the 4D level^{6,12}. The fact that very little enhancement of the latter peak occurs when the N_2 -laser is present might mean that the ionization induced by the dye laser and the collisions is nearly complete, or alternatively, that the cross-section for photoionization from the 4D-level to the continuum is small. The continuum signal observed with both lasers irradiating the flame disappears when the dye laser is blocked or when the N_2 laser is blocked. This indicates that the continuum signal is due to off-resonant two-photon ionization by both lasers.

D. Conclusions

We have shown that ionization of seed atoms in the flame can be achieved relatively simply by irradiating the atoms simultaneously with one resonant and one off-resonant laser pulse, both of which have a duration of a few nanoseconds. From the experiments conducted we conclude that the predominant mechanism for ionization proceeding from the Na(3P) level is two step

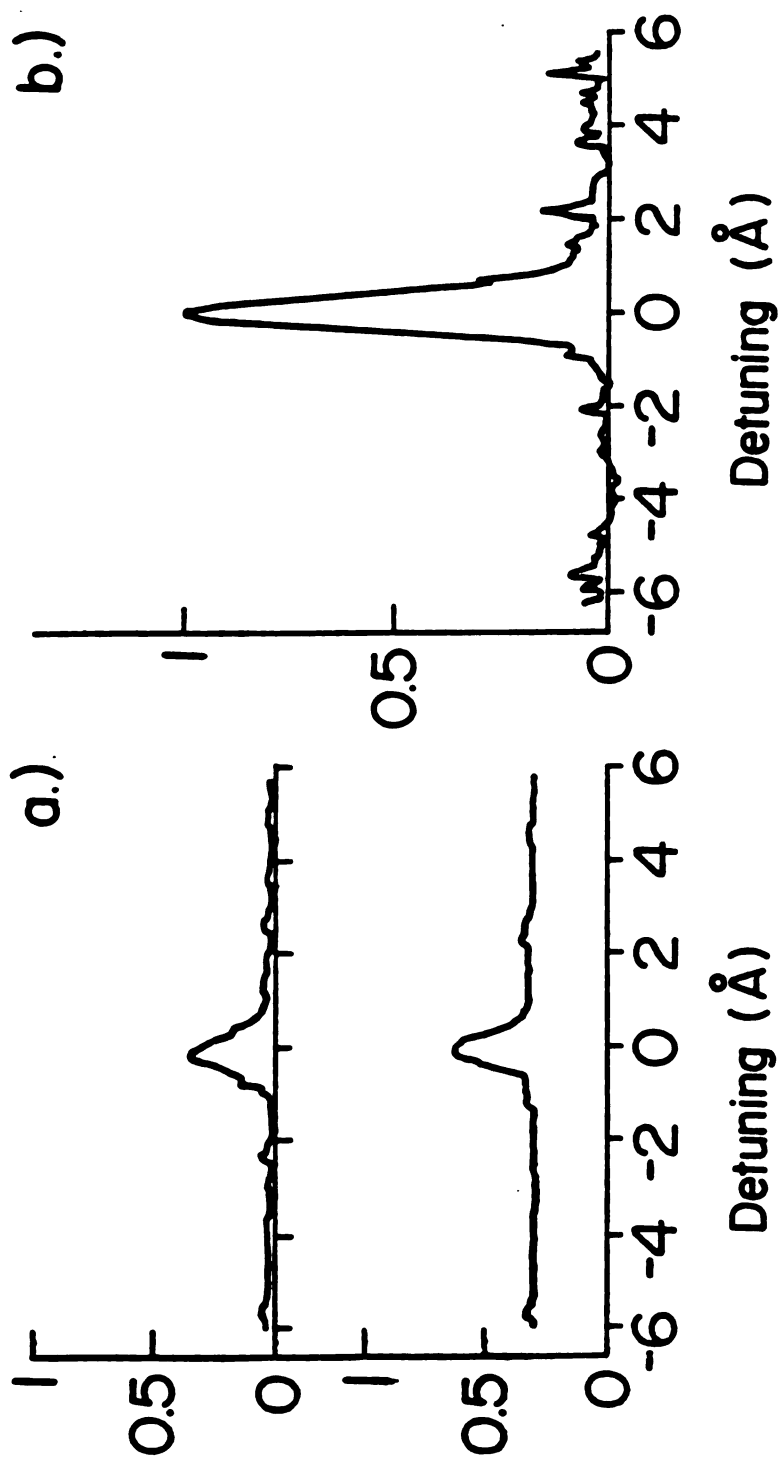


Figure A-6. Ionization profiles obtained by scanning the dye laser across the Na(3S → 4D) two-photon transition; center wavelength = 5787 Å, $R_0 = 50 \text{ k}\Omega$, $2\phi_p = 100 \text{ V}$; sodium solution concentration = 100 $\mu\text{g/ml}$. a) Upper trace: N_2 laser beam interrupted; lower trace: both the N_2 laser beam and the dye laser beam operative. b) Detailed profile.

photoionization; in the case of population of the Na(4D) level, collisions cause the excited atom to ionize. The described method to measure ion mobilities has been tested and been found to yield a value consistent with previous results.

Although the detection limits by the two-step method are not as low as those obtained by normal LEI¹² it is expected that perfection of this method will improve these limits. Feasible improvements are: using a slot burner and extended probes running parallel to the laser beam for several inches to increase the collection efficiency of the probes; using an ultrasonic nebulizer instead of our pneumatic nebulizer to increase nebulization efficiency; narrowing the bandwidth of the dye laser to increase its spectral irradiance.

E. Appendix

In this appendix we develop expressions for the mobility-controlled ion density in a flame. As an approximation to our experimental conditions we consider two parallel plane probes at a distance $2L$ from each other, with a voltage difference $2\phi_p$ applied to them by an external source. The probes are located inside the flame and the charge density is assumed to be uniform throughout the space between the probes when the applied voltage is zero.

We are interested in the case in which the distribution of the ions is primarily determined by the electric field; consequently, we neglect here diffusion, the overall movement of the flame gases, recombination, and ion production. The continuity equation for the ion density then reads

$$\frac{\partial n_i}{\partial t} = - \mu_i \nabla \cdot (n_i \tilde{E}), \quad (A1)$$

where μ_i denotes the ionic mobility and $\tilde{E}$ denotes the electric field. If the contribution of the laser induced charges to the field $\tilde{E}$ is small, then $\tilde{E}$ is nearly constant during a laser pulse. The latter assumption allows us to separate variables as follows

$$n_i(x, y, z, t) = N_i(x, y, z) f_i(t). \quad (A2)$$

Substituting enq. (A2) into eqn. (A1) gives

$$\frac{1}{f_i(t)} \frac{\partial f_i}{\partial t} = \frac{\mu_i}{N_i} \nabla \cdot (N_i \tilde{E}). \quad (A3)$$

Since the left hand side of eqn. (A3) depends on t only and the right hand side on the spatial variables only, we set both sides equal to a constant $-1/\tau_i$. The solution for $f_i(t)$ is found to be

$$f_i(t) = e^{-t/\tau_i} \quad (A4)$$

The equation for the steady state can be written as

$$\nabla \cdot (\alpha \tilde{\mathbf{A}}) = \alpha \nabla \cdot \tilde{\mathbf{A}} + \tilde{\mathbf{A}} \cdot \nabla \alpha \quad (\text{A6})$$

where α and $\tilde{\mathbf{A}}$ represent differentiable, but otherwise arbitrary scalar (α) and vector ($\tilde{\mathbf{A}}$) functions of the spatial coordinates, eqn. (A5) becomes

$$N_i \nabla \cdot \tilde{\mathbf{E}} + \tilde{\mathbf{E}} \cdot \nabla N_i - N_i / (\mu_i \tau_i) = 0 \quad (\text{A7})$$

If we assume that the field $\mathbf{E}$ is nearly uniform throughout the probed region, then

$$\mathbf{E} = - \phi_p / L. \quad (\text{A8})$$

If our attention is restricted to the one-dimensional case, then substitution of eqn. (A8) in (A7) gives

$$\frac{\partial N_i}{\partial x} = - N_i L / (\phi_p \mu_i \tau_i). \quad (\text{A9})$$

Hence

$$N_i = n \exp[-xL / (\phi_p \mu_i \tau_i)] \quad (\text{A10})$$

where n is a constant of integration. Thus, the ion density is highest near the negative probe and decreases in the direction of the positive probe (located at $x = + L$).

Identifying τ_i with the characteristic time it takes for an ion to drift from $x = 0$ to $x = - L$

$$L = -v_i \tau_i, \quad (\text{A11})$$

where v_i is the average drift velocity. In the limit of a

low, uniform field

$$v_i = \mu_i E. \quad (A12)$$

Combining eqns. (A8), (A11) and (A12)

$$\tau_i = L^2 / (\mu_i \phi_p) \quad (A13)$$

establishes a relation between the characteristic decay time and the ionic mobility in terms of the distance between the probes and the applied potential. Using eqns. (A10) and (A13)

$$N_i = n \exp(-x/L), \quad (-L < x < L) \quad (A14)$$

which agrees with the solution found for the so-called plasma-capacitor in the limit of low charge density¹⁴³.

Due to the absence of the diffusion term in eqn. (A5), the charge density does not obey the boundary conditions

$$N_i(\pm L) = 0.$$

*Obtained jointly with K.C. Lin and C.A. van Dijk.

APPENDIX B

APPENDIX B

DYE LASER DESCRIPTION AND ALIGNMENT PROCEDURE

A. Introduction

A tunable organic dye laser system of the design first described by Hänsch⁹³ was used in all the experiments. In this design a laser dye solution in a quartz cuvette is incorporated into a short optical cavity formed between a diffraction grating and a partially reflecting output coupler. The dye molecules, which function as the active material, are optically pumped by a repetitively pulsed nitrogen laser placed at a 90° angle to the cavity. Laser dyes are large multiringed organic structures which contain conjugated double bonds and absorb strongly in the ultraviolet. The energy levels of these molecules are wide, typically 1000 cm^{-1} to 2000 cm^{-1} , because line broadening processes in solution smear the rotational lines to a continuum around the vibrational lines composing the individual electronic states. Thus the fluorescence emission is broadband in nature, which allows the laser to be tuned. The wavelength fed back through the active region to initiate the laser action can be selected with the grating. The laser output consists of a train of short pulses of high intensity. Repetition rates up to

60 Hz are possible. Extremely low bandwidths can be obtained with the inclusion of additional wavelength selective elements (e.g. a Fabry-Perot etalon) if necessary. The large gain bandwidth also permits the generation of ultrashort (picosecond) pulses through mode-locking. The wavelength region from about 350 nm to 800 nm is accessible with currently available, high-gain laser dyes.

The remainder of this Appendix consists of a description of the components of our optical system and their functions followed by the alignment procedure for the dye laser.

B. Optical System Components

A block diagram of the entire laser system is given in Figure B-1. The laser cavity is formed by a diffraction grating and a quartz output coupler. The grating was mounted backwards on the sine-bar of a Czerny-Turner grating monochromator (Model EU-700, GCA/McPherson Instruments, Acton, MA) to provide for the rotation needed for tuning. The monochromator sits on an aluminum table equipped with three independently adjustable legs. The table is positioned so that it is directly above the optical rail that holds the rest of the dye laser cavity components. The precision plane grating replica used was the standard grating available with the monochromator (48 square millimeter ruled area with 1180 lines/mm). The blaze wavelength was 250 nm. This grating was adjusted on the

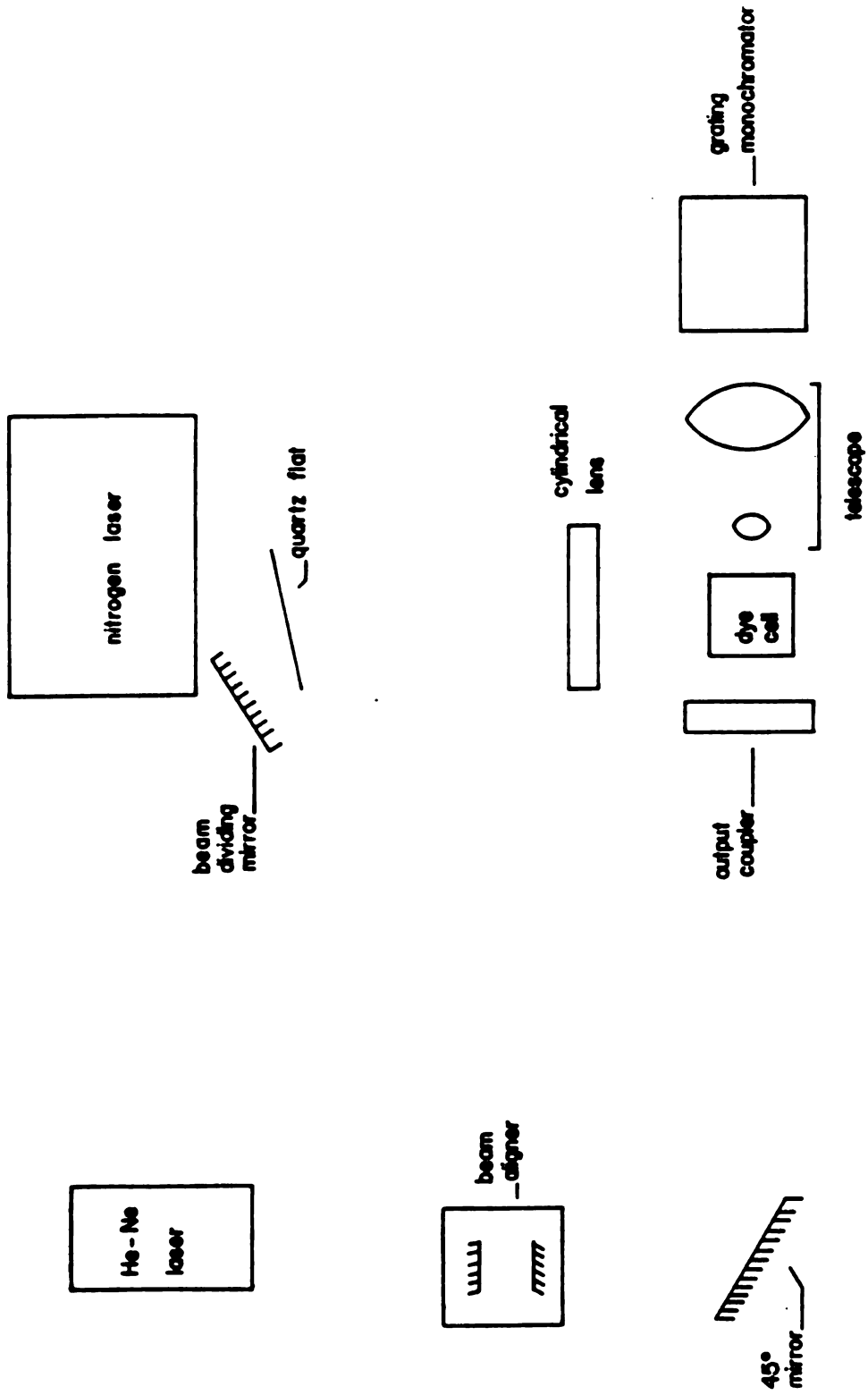


Figure B-1. Block diagram of laser system.

sine-bar so as to operate in the second order (see alignment procedure section-step 12). A 4% reflective quartz flat (1 inch diameter) was used as an output coupler for all of the experiments performed. This flat was mounted in a three point adjustable holder attached to a pole that was fixed in a mount riding on the optical rail. The distance between the ends of the cavity varied from alignment to alignment but was always between 30 and 35 cm. The dye laser cuvette had four quartz sides with single layer antireflection coatings. The two sides perpendicular to the cavity were offset at a slight angle to prevent them from acting as cavity end mirrors. This cuvette was obtained from a commercial source (Type 509, Precision Cells, Inc., Hicksville, NY) and had a path-length of 8 mm. It was mounted in a Delrin holder on an aluminum frame and attached to the optical rail in a fashion similar to the output coupler. The frame slides on a dovetail to give adjustability across the rail. Also, the frame is fitted with a small DC motor with a magnetic stirring bar attached to the shaft. The bar can spin freely under the Delrin holder. This arrangement was constructed to provide mixing of the dye solution with a miniature magnetic stirring bar immersed in the dye solution. Studies indicated, however, that stirring causes vibrations which can misalign the cuvette; thus use has been discontinued. The motor controller circuit has been described elsewhere¹⁰⁰. No further attempt at mixing was

made because the output stability of the dye laser was deemed sufficient for the experiments performed. The final cavity element is the inverting telescope (Model 1592, Oriel Corp., Stamford, CN), which collimates and expands the incoming beam so that it nearly fills the grating. The Galilean design incorporates a diverging input lens (in the final configuration this has a focal length of -4 mm) and a converging output lens with a focal length of 160 mm. The mount, attached directly to the optical rail, provides adjustment both horizontally and vertically (across the rail). Also micrometer drives provide "tilt" (i.e. angle tuning) in both the horizontal and vertical planes.

A 5 mW randomly polarized helium neon laser (Model 05-LHR-151, Melles Griot, Irvine, CA) is mounted on an optical rail at 90° to the laser for cavity alignment. The mount is a nine inch V-groove to accommodate easy removal and replacement. The beam is brought to the cavity with a commercially available, two mirror, laser beam aligner (Model 6650, Oriel Corp., Stamford, CN). To direct the beam down the cavity a flat mirror held in a 3-point adjustable mount is placed on the optical rail containing the cavity components.

To bring the nitrogen laser pumping beam to the dye cuvette a quartz optical flat (2 inch diameter) and a cylindrical lens are used. The flat changes the beam spread to the cylindrical lens and is a coarse adjustment

only. The cylindrical lens is set in a circular Teflon holder and this is then placed in a three-point gimbal mount. The Teflon holder can be rotated 360° . This entire arrangement is mounted to provide motion in three dimension.

C. Alignment Procedure

The following procedure assumes that all the dye laser components are completely misaligned, including those involved in directing the nitrogen beam to the dye cuvette. A number of the steps (denoted by asterisks) can be omitted if some components are known to be aligned. All components are set in mounts (many atop poles) that are free to slide on the optical rails. The target referred to is a square card, with measured markings, attached to a pole set in a rail mount.

1. Remove all components from the dye laser optical rail.
- *2. Start the nitrogen laser and adjust (either with nitrogen laser table legs or with cylindrical mirror mount) the beam direction so that the beam strikes the cylindrical lens in the center.
3. Place the target on the optical rail and turn the face 90° so that the beam (nitrogen laser) strikes it. Adjust the height of the target so the cylindrical beam, when focused, falls on the horizontal cross hair. This will be the height of the center of the cavity.
4. Turn off the nitrogen laser, rotate the target face back and turn on the He-Ne laser.
- *5. Make sure that the He-Ne laser beam is striking the lower mirror of the laser beam alignment unit.

6. Place the reflecting mirror on the dye laser optical rail so that it forms roughly a 45° angle with the rail and so that the alignment beam strikes it. If the mirror is at 45° , the beam should be directed down the rail (roughly-finer adjustments will follow).
7. Move the target to a position approximately 3 inches from the 45° mirror, and use the laser beam aligner to adjust the beam so that it strikes the target in the center.
8. Move the target to the other end of the cavity (about 2 inches in front of the grating).
9. Use a screwdriver to adjust the mirror mount so the beam is centered once again on the target (this may take more than one attempt as the 45° mirror may have to be moved slightly or twisted). Then return the target back to its earlier position near the 45° mirror to make sure the spot is still centered. If not, repeat steps 7-9.

Upon completion of step 9 the He-Ne laser is directed straight down the rail and the dye laser components can now be aligned with it.

10. Remove the target from the rail and adjust the position of the grating (by sliding the monochromator on its table) so that the beam strikes it roughly in the center.

At this point the grating must be aligned in the second order with the wavelength selector set to allow a sufficient tuning range. With the grating reversed on the sine-bar and operating in the second order, a change of approximately 2.5 Å on the wavelength counter equals a change of 1 Å in the laser output wavelength. Since the He-Ne laser line at 6327 Å is used, the cavity will be aligned at this wavelength at the end of the procedure. For the laser to lase at 4000 Å, approximately the lowest wavelength normally used, the wavelength counter must be free to move,

in a downward direction, a number of Angstroms given by

$$(6327-4000) \times 2.5 = 5818 \text{ \AA}$$

Similarly to lase at the approximate upper limit of 7500 Å the counter must be free to travel about 2930 Å upwards. As the full counter range is 10,000 units, an initial wavelength selector setting of 7000 Å will cover the entire useful range.

11. Set the wavelength selector to 7000 Å.
- *12. Set the grating angle so it is operating in the second order. Loosen the screw on the sine-bar (near the grating holder) so the grating is free to pivot. Twist the grating so the second order reflection is directed down the cavity (to be sure, count the orders: the zero order reflection will be stopped by the stray light shield between the grating and the folding mirror. The first order reflection will miss this and can be viewed either on the wall or on a card held near the grating. The next reflection is the one wanted for cavity alignment).
- *13. Tighten the holding screw.
- *14. Loosen the monochromator holder and translate (slide) the monochromator on the table so that the alignment beam is hitting the grating in the center.
15. Make minor table leg adjustments so the second order reflection is collinear with the incoming beam.

The grating is now aligned with the He-Ne beam.

16. Attach the telescope mount to the rail so that the telescope output lens is about 5 cm from the center of the grating.
17. Use the course (non-micrometer) adjustments on the telescope mount to position the telescope so that the alignment beam strikes the 4 mm input lens; then remove this lens.

18. With the lights out, two diffuse (blurry) spots will be seen in the far field (i.e. a card near the 45° mirror). Use the micrometer drives to bring these together.
19. Insert the 16 mm input lens. A card held behind the 45° mirror will show a large spot of light. Slide the output lens sleeve so that this focuses to a pinpoint. A bright area, 2-3 cm in diameter, should now be visible on the grating. Use the course adjustments to move this to the grating center, and then use the micrometer drives to direct the pinpoint so it falls on the alignment beam spot on the 45° mirror.
20. Replace the 16 mm lens with the 4 mm lens. The spot on the grating should be larger and dimmer than before (in fact, will more than cover the grating). A card behind the 45° mirror will once again show a large spot which should be focused as much as possible (although this will not focus to a pinpoint as before). Once again, position the spot, with the micrometer drives, to hit the reflection of the alignment beam on the 45° mirror.

The telescope is now aligned as much as possible at this point. Minor adjustments will be needed later. (Note: the diffuse reflected beam found with the 4 mm lens is sometimes difficult to find behind the 45° mirror. It is because of this that the 16 mm lens is used for "rough" initial alignment. If there is still difficulty, there is an 8 mm input lens that can be inserted after the 16 mm lens is removed (i.e. repeat step 20 but with this 8 mm lens). This will make the step down easier but more tedious.)

21. Place the output coupler on the rail 30 cm to 35 cm from the grating. Adjust the mount so that the reflection lines up with the incoming beam.
22. Place the cuvette holder on the rail so that the cuvette is in front of the cylindrical lens that directs the nitrogen laser beam into the cavity.

23. As the nitrogen beam only excites a small volume near the first quartz face that it strikes, it is necessary that the He-Ne beam go through this area. Move (slide) the cuvette across the rail so that the He-Ne beam is as close to this face as possible.

The cavity should now be aligned at the He-Ne laser wavelength. Set the wavelength counter to a reading appropriate for the dye in use. For example, if you want to use Stilbene 420 which, in methanol, has a maximum in its laser gain band at 425 nm, the wavelength counter setting is given (approximately) by

$$7000 - (6327 - 4250)(2.5)$$

and thus should be 1808 Å. For other dyes the start up setting is obtained simply by replacing 4250 in the above equation with the wavelength of maximum gain for the dye of interest.

24. After setting the wavelength counter to the appropriate reading (see above), start up the N₂ laser and hope for the best. The laser will probably not lase at once and small cavity adjustments may be necessary. First make sure the cylindrical lens is focused near the inside wall of the cuvette.
25. A card held in front of the input lens of the telescope will show a bright spot from the dye solution. This should strike the 4 mm lens (i.e. fall on the same area as the alignment beam). If it doesn't use the mount of the cylindrical lens and/or twist the dye cuvette slightly so that it does.
26. If the laser still is not lasing use the micrometer on the underside of the telescope to adjust the horizontal tilt angle. A card held behind the output coupler may show a reflection that is not a spot but a dim line. This should be brought down so it is even with the alignment laser. At this point laser action is almost always achieved. Once laser action is found it can be improved by

making minor adjustments to the end mirror, telescope, etc. The pure, sometimes grainy, reflection on the grating (at the dye laser wavelength) can be seen and centered.

27. Reflected laser light may appear as a spot near the main laser spot. This can be removed (if necessary) by placing a diaphragm in the cavity. This is usually taped to the output coupler mount.

APPENDIX C

APPENDIX C

LOCK-IN AMPLIFIER DESIGN

A. Introduction

A lock-in amplifier is often used to enhance signal-to-noise ratios (S/N) in spectrometric measurements. Typically, the slowly varying dc signal generated by the experiment is used to modulate the amplitude of a carrier wave which has a frequency well removed from dc where $1/f$ noise can predominate. The lock-in amplifier then selectively amplifies the signal, synchronously demodulates it by multiplication with a bipolar reference square wave of equal frequency and phase and finally low pass filters it. The output, then, is an amplified version of the input. Lock-in amplifiers have been described in more detail by Malmstadt, Enke and Crouch¹⁴⁴.

A lock-in amplifier system, which is a modification of a design given by Holler, et al.¹⁴⁵, is described in this Appendix. The design is simple and inexpensive as it involves only three integrated circuits other than common operational amplifiers. Still, the lock-in amplifier is versatile enough to handle signals generated in all common laboratory experiments such as atomic

absorption, thermal emission, etc. Carrier frequencies between 10 and 10,000 Hz can be used. The unit is intended for use with the atomic absorption spectrophotometer described in chapter VI. This atomic absorption instrument uses a carrier frequency of 285 Hz. Because of this, the tests of the lock-in amplifier described in this Appendix were performed at this frequency.

B. Design Considerations

B-1. General

The simplified circuit for the lock-in amplifier is shown in Figure C-1 and the detailed schematic is shown in Figure C-2. The basic design consists of a signal channel for tuned amplification of the modulated carrier wave, a reference channel to provide a bipolar, phase-shiftable square wave, a multiplier for synchronous demodulation and a low pass filter to provide a (amplified) dc output. All of the operation amplifiers (op amps) used were common single IC dual op amps (either Model TL082, Texas Instruments, Inc., Dallas, TX or Model LF353, National Semiconductor Corp., Santa Clara, CA). Both the reference and signal channels employ AF100 universal active filters (National Semiconductor Corp., Santa Clara, CA). These are configured similarly and described together.

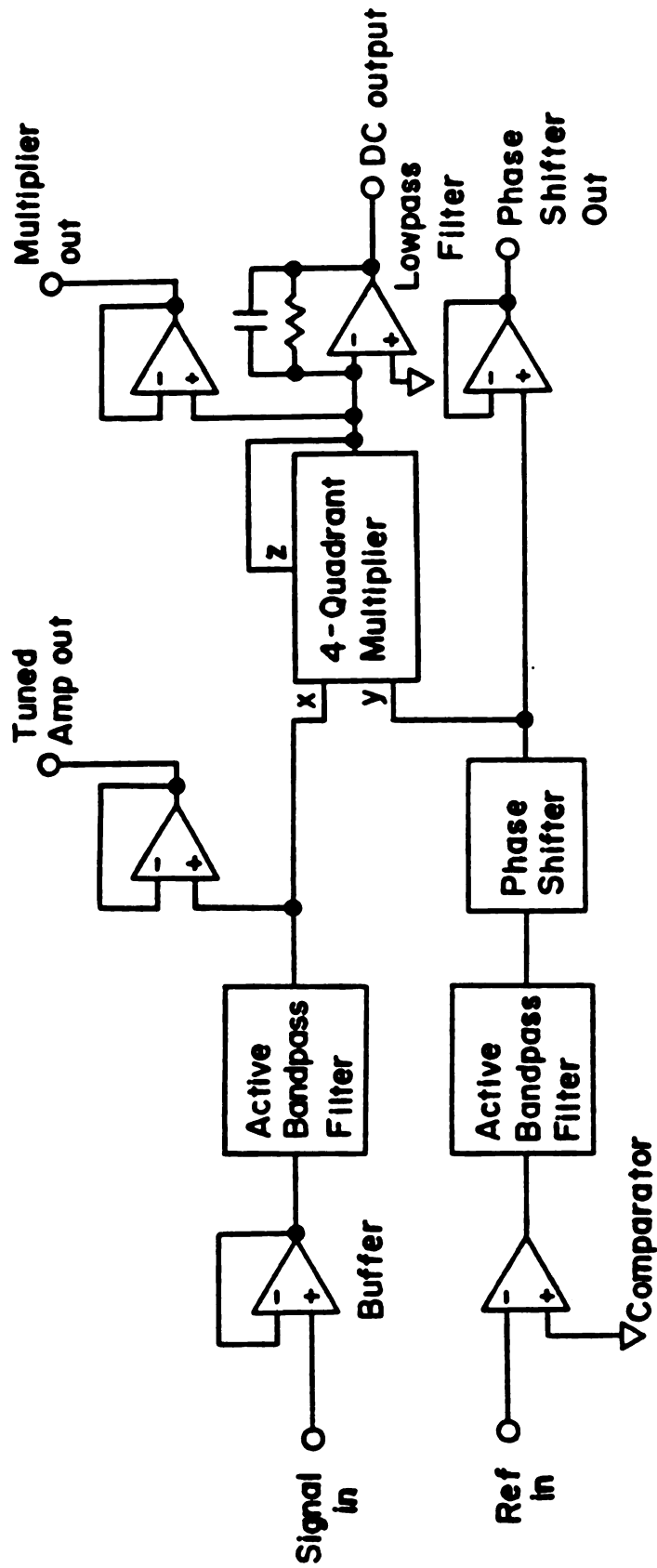


Figure C-1. Simplified circuit diagram for lock-in amplifier.

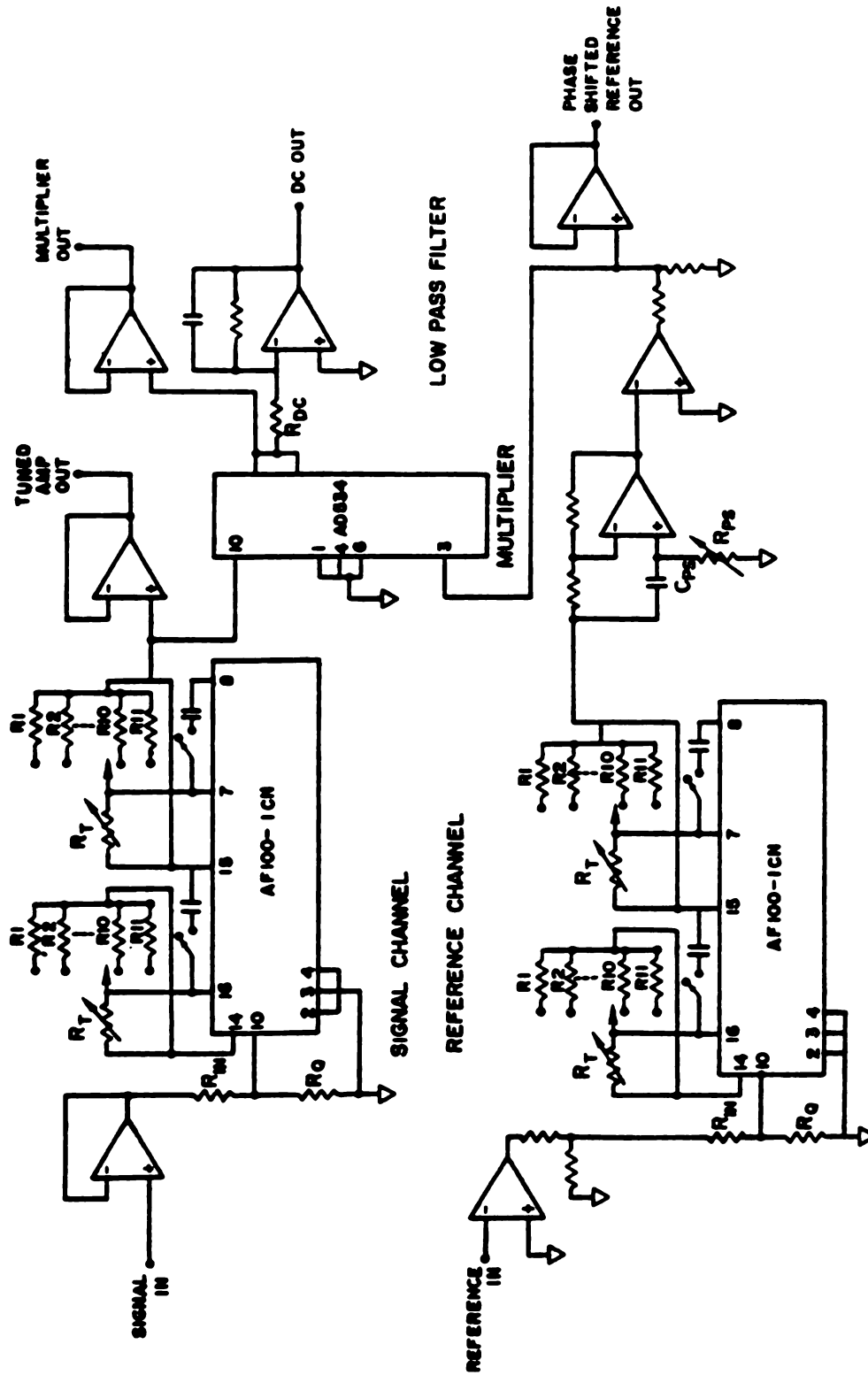


Figure C-2. Detailed circuit diagram for lock-in amplifier.

B-2. Inputs

The modulated carrier is the input to the signal channel through a simple voltage follower buffer. The reference signal is connected to a comparator followed by a voltage divider. With this type of input even low level signals can be used for the reference since the comparator (with the non-inverting input grounded) will produce a bipolar square wave of approximately ± 15 V. The voltage divider (3:1) then reduces this to a usable ± 5 V.

B-3. Active Filters

The active filter in the signal channel acts as the tuned amplifier to selectively amplify the modulated carrier wave. In the reference channel the active filter converts the reference square wave to a sine wave. This is necessary as the phase-shifting circuit works only on sine waves. The AF 100 filters are identically configured and operated in the band pass mode. To tune the center frequency of the filter two resistors are used, one between pins 7 and 15 and one between 14 and 16. The tuning range of the basic filter is 200 to 10,000 Hz. Lower frequencies (to dc) can be obtained by inserting capacitors between pins 7 and 8 and 15 and 16. To provide continuous variability in the filters, variable potentiometers were used in parallel with switch-selectable fixed resistors. This arrangement was used to maximize the frequency selectivity as for each range of frequencies almost the entire range of the variable

resistor is used. Since the frequencies of the AF 100 filters in each channel must tune simultaneously, a four level modular potentiometer was used. This was assembled from two modular potentiometers purchased from a commercial source (Series 70 "Mod Pot", Allen-Bradley Co., Milwaukee, WI). Each of the four modules has a 250 k Ω tuning range and the unit was equipped with a 16 turn verneir drive for separability. The parallel, fixed resistance was chosen with a 4 pole, 4 section, 11 position rotary switch (Series 1400, Centralab, Inc., Menomonee Falls, WI). The fixed resistors were matched. The switch positions, frequency ranges and fixed resistance values are listed in Table C-1. For ranges below 200 Hz a 4 pole double throw switch was used to connect the capacitors (.022 μ F). For frequency ranges above 200 Hz the center frequency of the filter is given by

$$f_0 = 50.33 \times 10^6 / R$$

and below 200 Hz by

$$f_0 = 0.05033 / R(0.022 \times 10^{-6} + 1 \times 10^{-9})$$

where R is the value of the tuning resistance. The quality factor of the filter, Q, determines the band-pass of the filter. Q is determined by the value of the input resistor (R_{IN}) and the Q tuning resistor (R_Q). These values were chosen to be 5 k Ω and 1 k Ω respectively.

TABLE C-1. Frequency Ranging Data.

<u>Switch Position</u>	<u>Frequency Range (Hz)</u>	<u>Fixed Resistance (kΩ)</u>
1	10-20	none
2	20-40	200
3	40-80	75
4	80-160	32.4
5	160-200	14.7
6	200-400	none
7	400-800	261
8	800-1600	90.9
9	1600-3200	38.3
10	3200-6400	16.8
11	6400-10,000	8.25

in the filter configuration used this gives a Q of approximately 35. At the 285 Hz test frequency, the band-pass (from upper to lower 3dB points) with this Q is 281-289 Hz.

B-4. Phase Shifter

The circuit used to adjust the phase of the reference wave to match that of the signal is a constant-amplitude phase shifter which has been described elsewhere¹⁴⁶. In this a ten turn potentiometer (100 k Ω maximum value) is varied to determine the amount of shift. To function properly the input must be a sine wave; the output of the circuit is also a sine wave. In order to regenerate a square wave, which produces optimal results upon multiplication with the signal channel output, the output of the phase shifter is directed to a comparator followed by a 3:1 voltage divider.

B-5. Multiplier

The outputs of the signal and reference channels are input to a four quadrant multiplier (AD 534, Analog Devices, Norwood, MA). This provides the synchronous demodulation of the carrier wave through cross-correlation. This strongly discriminates against random noise which is not in phase with the signal and reference waves. The output of the multiplier is a full wave rectified sine wave whose amplitude is proportional to the input signal.

B-6. Low Pass Filter

The output of the multiplier was fed through a low filter to produce a "smoothed" dc level proportional to the input signal. The time constant of this filter was chosen to be 1 second for the tests to be described in section C. The final version of the amplifier (now under construction) will have a variable output time constant.

B-7. Outputs

As this lock-in amplifier was intended for use in an instructional laboratory situation, a number of outputs in addition to the normal dc output were provided. The outputs of the tuned amplifier, the multiplier and the reference channel were all buffered and taken to BNC connectors on the case.

C. Testing

To test the lock-in amplifier a signal was generated by pulsing an LED with the TTL output of a function generator. This was detected by a photodiode whose output was fed to a current-to-voltage (I/V) converter. To add noise to the signal output of a noise generator circuit based on the 5837 digital noise generator IC was used. This type of signal source has been described in more detail elsewhere¹⁴⁵. The output of this circuit was connected to the signal channel input. The reference wave was obtained from the bipolar square wave output of the function generator. The reference channel was

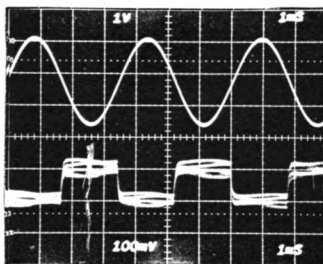
found to work as expected for input peak-to-peak square wave amplitude as low as 20 mV.

For initial tests the function generator was set to 285 Hz, and the noise generator circuit output was disconnected. A series of photographs of the various inputs and outputs of the lock-in under these conditions are presented in Figure C-3. Figure C-3a shows the actual input signal (lower trace) and the output of the tuned amplifier (upper trace). The fluctuations in the input signal were caused by the room lights. These were strongly attenuated by the tuned amplifier. The data also show a linear gain in this step of approximately 25 (30 dB). The upper trace in Figure C-3b shows the output of the reference channel and the lower trace shows the output of the multiplier (in-phase condition). Finally, the actual dc output is shown by the upper trace of Figure C-3c. The lower trace is the baseline or "signal blocked" condition.

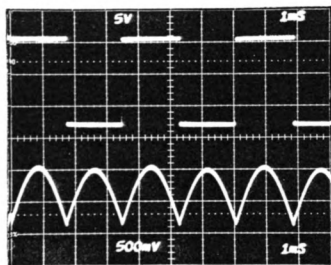
Shown in the series of photographs in Figure C-4 are the same series of measurements with the noise generator connected. The lower trace of Figure C-4a shows the signal buried in random noise (~ 0.8 V p-p). As the original input signal was on the order of 0.1 V the input S/N ratio was about 0.125. The upper trace shows the output of the tuned amplifier. The reference wave is once again shown in Figure C-4b along with the

Figure C-3. Lock-in amplifier without noise. (a) lower trace: signal channel input; upper trace: output of tuned amplifier. (b) lower trace: output of multiplier; upper trace: output of reference channel. (c) lower trace: dc output with signal "blocked"; upper trace: dc output with signal "open".

a)



b)



c)

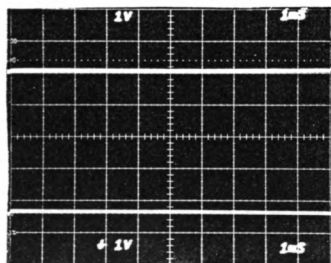
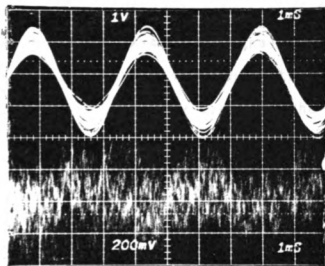


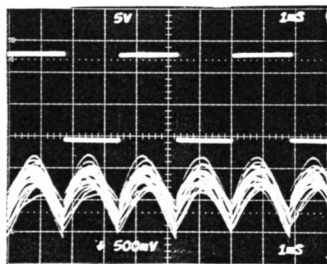
Figure C-3.

Figure C-4. Lock-in amplifier test with noise. (a) lower trace: signal channel input; upper trace: output of tuned amplifier. (b) lower trace: output of multiplier; upper trace: output of reference channel. (c) lower trace: dc output with signal "blocked"; upper trace: dc output with signal "open".

a)



b)



c)

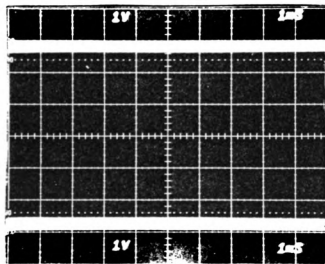


Figure C-4.

output of the multiplier. Finally, in Figure C-4c the dc output is shown. From this, the signal was measured as 5.6 V. The peak-to-peak noise on both the upper and lower traces is approximately 0.4 V so the actual noise in the measurement can be estimated as 0.56 V. The S/N, then, has been increased to 10 so the total S/N enhancement by the lock-in amplifier was 80.